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MODERN TRENDS IN ACTIVATION ANALYSIS

Proceedings of the 1968 International Conference
held at the National Bureau of Standards
Gaithersburg, Maryland, October 7–11, 1968

James R. DeVoe, Editor
Philip D. LaFleur, Assistant Editor

Institute for Materials Research
Analytical Chemistry Division
National Bureau of Standards
Washington, D.C. 20234

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ABSTRACT

A conference on Modern Trends in Activation Analysis was held at the National Bureau of Standards, October 7–11, 1968. This volume contains texts of two invited plenary lectures, one on the applications of activation analysis and one on radiochemical separations, contributed papers, remarks by honored guests, and synopses of discussion sessions by each chairman. Topics covered include applications of activation analysis in the environmental sciences, biology, medicine, archaeology, criminology, geochemistry, geology, and industry. Also included are studies on radiochemical separations.

Key Words: Conference, activation analysis, applications, nuclear reactions, neutron, charged particles, photons, radiochemical separation, geochemistry, biology, industry, criminology, archaeology.

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FOREWORD

The Analytical Chemistry Division of the NBS Institute for Materials Research provides a major national focal point for analytical chemistry through its continuing efforts to encourage meaningful analytical measurements, to exercise leadership in attacking analytical problems of the nation, and to fill in gaps in critical measurement competences. This Division consists at present of about 120 technical personnel encompassing some 57 different analytical competences from activation analysis and atomic absorption to vacuum fusion and x-ray spectroscopy. These competences are charged with the responsibility for research at the forefront of analysis as well as for an awareness of the practical sample, be it Standard Reference Material or service analysis.

One important mechanism by which the Division exercises leadership in the "state of the art" of a competence is that of sponsoring special conferences and symposia. Experts from around the world are invited to these conferences to summarize the present status of the many facets of a particular competence. In addition, contributed papers as well as comments of rapporteurs or summaries of panel discussions are often used to help better define this status.

The first such conference sponsored by the Division was a broad one on "Trace Characterization—Chemical and Physical" held October 3–7, 1966 at the new NBS Laboratories at Gaithersburg, Maryland. On June 12–13, 1967, a seminar on a more restricted topic, "Quantitative Electron Probe Microanalysis," was held in these same facilities. The hard-cover proceedings of each of these meetings are available from the Government Printing Office as NBS Monograph 100 and NBS Special Publication 298, respectively.

As a continuation of these definitive "state of the art" conferences, the Analytical Chemistry Division and the NBS Institute for Materials Research were very pleased to host the 1968 International Conference on Modern Trends in Activation Analysis. These volumes are the end product of the 1968 conference and contain the plenary lectures as well as condensations of the more than 150 papers submitted. We hope that the volumes will provide the reader, be he specialist or generalist, with a definitive, up-to-date picture of this very important field of activation analysis.

The excellent organization provided by James R. DeVoe, Philip D. LaFleur, and their many associates for this week-long conference made available a maximum amount of time for very substantive discussions in the broad field of activation analysis. Dr. DeVoe's tireless efforts in organizing and editing the papers for this conference provided the primary drive which resulted in an outstanding conference and in pertinent, up-to-the-minute proceedings. Special thanks are due Mrs. Rosemary Maddock whose continuing interest in, and awareness of, the rapidly changing techniques for literature publication have made possible the early issuance of the proceedings of all our conferences.

W. Wayne Meinke, *Chief,*
Analytical Chemistry Division,
Institute for Materials Research.

PREFACE

The third in a series of conferences on activation analysis, "The 1968 International Conference on Modern Trends in Activation Analysis," was held at the National Bureau of Standards, Gaithersburg, Maryland on October 7–11, 1968. The conference, which was sponsored jointly by the National Bureau of Standards, U.S. Atomic Energy Commission, International Atomic Energy Agency, and EURISTOP, European Communities Commission, was truly an international one with one-third of the attendees coming from thirty-two different foreign countries. The scope of the conference was comprehensive in the sense that fundamental studies were combined with as many applications as could be conveniently accommodated. It is an almost obvious fact that the field of activation analysis has grown to a point where such comprehensiveness will be very difficult to achieve in any future conference of five days' duration.

The format for the conference was designed to maximize efficiency in transmitting the large volume of information associated with this field. Authors were encouraged to make liberal use of figures and tables for the preparation of the condensations which appear in these proceedings. These condensations were then made available to the attendees one week prior to the beginning of the conference in a preprint booklet.

Although each condensation was carefully edited and the author's corrections have been made, questions resulting from the absence of the usual "refereeing system" may arise. All authors of condensations are encouraged to publish their work in greater detail in a formal scientific periodical of their choice.

Each day of the conference began with a "state of the art" plenary lecture on a major phase of the activation analysis technique. In order to provide complete coverage of the field, simultaneous sessions were required. The regrettable problem that the attendee faced in wanting to be in two places at once was alleviated to some degree by convening a plenary panel discussion at the end of each day in which all of the chairmen of the day's sessions provided a synopsis of the major points of discussion in their particular session. Synopses of these discussions appear in these proceedings.

The availability of highly efficient business machines when combined with the format for this conference, provided for rapid publication of the proceedings (which is a necessity if conference proceedings are to have any useful purpose). All of the papers were typed on a typewriter that was connected to a magnetic tape recorder. The typewritten copy was reproduced to create the preprint. Authors were asked to edit their paper in the preprint. These corrections along with properly coded instructions were entered onto the previously recorded tape. This tape was then converted to a computer-compatible tape which was formatted to be processed through an automated typesetting system, with graphic-art quality, at the Government Printing Office. Since uncorrected parts remained unchanged on the tape, the author's correction of the preprint constituted editing of galley proofs which was essentially completed by the end of the conference! Such efficiency in documentation has resulted in proceedings which contain the invited plenary lectures, the submitted condensations of papers, and the synopses of discussions in the sessions, and these extend through two volumes. A "personnel register" of persons working in the field of activation analysis will be published separately.

We were most fortunate to have Dr. Glenn T. Seaborg, Chairman of the U.S. Atomic Energy Commission address the conference on October 11, 1968. His remarks provide a most suitable preamble for this volume of the proceedings.

Conducting a conference of this magnitude could not have been done without the assistance of many people within the National Bureau of Standards. Many of these are included in the list of committees in Appendix I.

Special thanks is given to Dr. Philip D. LaFleur, Assistant General Chairman and editor, who very capably handled all of the arrangements for conducting the conference with the assistance of the NBS Office of Technical Information and Publications. His help and that of his Activation Analysis Section in checking proofs are also greatly appreciated.

The automated document processing was the result of cooperation between many groups at NBS: Mr. Rubin Wagner and Mrs. Rebecca Morehouse, who coordinated the transition from our code to that usable at the Government Printing Office; Mr. J. D. Waggoner, Mr. R. Thompson, and Mr. William O'Neal, who wrote various parts of the computer programs used; and of greatest importance, Mrs. M. Oland and Mrs. J. Gossard who spent long days of continuous effort in typing to meet deadlines and in assembling the preprints and encoding them for computer processing. Thanks is also given to Mrs. Joy Shoemaker and Mr. Robert Boreni for preparing the many tables and figures. Particular appreciation is expressed to Mrs. Rosemary Maddock who provided overall coordination of the procedures and assembly of the various parts of the preprints and proceedings that resulted in the high quality of documents that are hereby published.

By no means of least importance was the support (financial and otherwise) given by the Division of Analytical Chemistry, Dr. W. Wayne Meinke, Chief.

JAMES R. DEVOE.

November 27, 1968

1968 International Conference on Modern Trends in Activation Analysis

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Remarks by Glenn T. Seaborg

U.S. Atomic Energy Commission
Washington, D.C.

Thank you, Wayne. I think maybe it's a little late in the conference to make welcoming remarks, but I would like to say a few words anyway and maybe even reminisce for a moment about the way the field has developed in the last thirty years since we performed our first activation analysis experiment at Berkeley. The field has progressed a long way in that time. I was just handed a book of the abstracts for just this meeting, and I looked at the program and certainly was impressed with the types of determinations that can now be made through the activation analysis technique. I think that Wayne and those working with him have certainly succeeded in putting together a broad-ranging, interesting program here, one that must have entailed a lot of work in order to put it into effect, but I am not surprised. I had the privilege of having Wayne Meinke as my graduate student. He did his Doctor's degree work with me, and he was probably the hardest working and just about the most productive graduate student I had among all those in my teaching career. I was certainly glad to see that his efforts have been recognized by his receipt of the first George Hevesy Award of the Journal of Radioanalytical Chemistry. It is certainly a well deserved honor.

As I indicated, we did our first activation analysis experiment thirty years ago in 1938. And I believe that Jack Livingood and I conducted the first activation analysis experiment that was performed anywhere with charged particles. We used the cyclotron of E. O. Lawrence and I guess it was the first published activation analysis experiment of any kind performed in the United States. This was just a couple of years after the first neutron activation analysis experiments had been made in Europe. Jack Livingood and I were in the process of trying to identify a number of isotopes throughout the periodic table and we kept turning up extraneous activities, even though we used the purest targets available. I can remember in particular that we were bombarding iron with deuterons and we found activities of about 20 minutes half-life and 14 hours half-life in about the same intensity as the 47-day iron activity that we are trying to characterize. We were also looking to see if there were any other iron activities in addition to the iron-59. In puzzling about this, I recall that there were a 20 minute activity and a 14 hour activity that would be induced in gallium by deuteron bombardment. I had made a chemical purification of the iron previously in this case by extracting ferric ions into ether from 6N hydrochloric acid. However, gallium would have accompanied the iron in this extraction. I then reduced the iron and repeated the ether extraction, with the iron staying in the aqueous phase. The activity transferred to the ether, proving that it was gallium. We deduced that just a few parts per million of gallium would account for the activity observed.

We also detected the presence of a small amount of copper in nickel as the result of our neutron bombardments and a small amount of iron in cobalt as a result of our deuteron bombardments. Phosphorus-32, indicating the presence of small amounts of phosphorus, appeared in just about everything we bombarded. We then calculated the approximate concentrations of these impurities and I decided that I should turn what had been basically a nuisance and a disadvantage into an actual advantage. I wrote a paper for publication in the Journal of the American Chemical Society, pointing out how it was possible to detect very small amounts of radioactivity through the activation analysis technique. In fact, I think we called this first paper "Artificial Radioactivity as a Test for Minute Traces of Elements".

Now as I have indicated, things have progressed a tremendous distance since those first early experiments. I know that over the intervening years in my discussions of the peaceful uses of atomic energy, I have mentioned activation analysis techniques and what could be done with them in a number of instances. In a couple of cases, I have illustrated my point with some humorous anecdotes. I had lunch with some of the people in attendance here a few minutes ago and I was recalling that when George Hevesy received the Atoms for Peace Award in New York in 1959, and when I was privileged to be the speaker who recounted his achievements, I mentioned the story concerning Hevesy's boardinghouse in Copenhagen. I don't know whether you have heard that story or not, but it goes as follows: He became suspicious that the unconsumed meat that left the table one night came back to the boardinghouse table the following night as hash. In order to confirm this, he put a little bit of radioactive tracer on the unconsumed meat on his plate and sure enough the radioactive tracer showed that that same meat came back as the hash the following night. I told that story in the presence of George Hevesy, who was there, of course, to receive his award, and was interested to have it confirmed, after I spoke, that this story was essentially true. He had performed this experiment in a boardinghouse in Copenhagen in about 1913.

As I sat next to Dr. Lenihan today, I asked him if the other story that I have been telling was true, namely that through activation analysis it had been possible to establish the presence of arsenic in Napoleon's hair. He confirmed to me that arsenic had been found in Napoleon's hair and he told me about a number of other instances, such as the establishment of the presence of mercury in the hair of Charles the Second of England, and arsenic in the remains of Eric the Fourteenth of Sweden. I might say that if any of you have stories of that type that might embellish any of the many speeches I have to make, I would be glad to update my stories with these, and at the same time, perhaps do some good in publicizing what your field can accomplish.

I notice on the list of papers that were presented here one by Reinig and Evans on the isotope that has such new and exciting prospects for activation analysis, californium-252. This is an isotope in which I have special interest. I hope that the U.S. Atomic Energy Commission will be able to develop a program for the production of californium-252 in gram quantities, and maybe in the future in 10 and 100 gram quantities. This material has the potential for many applications in the future. As you know, it emits through the spontaneous fission process about 2×10^{12} neutrons per second per gram, so that it is almost equivalent to a small nuclear reactor. It makes possible a great number of uses for activation analysis and neutron radiography. For example, I visualize the use of portable californium-252 sources in mineral exploration. It may also have applications in cancer therapy and other medical uses. I think that this may be one of the real isotopes of the future for your field, and to illustrate the interest that has already been created in it, there is going to be a day-long symposium in New York a week from Tuesday, on October 22, in which the properties and uses of californium-252 will be the subject of discussion. I will speak at the symposium and will make some important announcements concerning the AEC's plans concerning the immediate and future availability of this isotope.

Wayne, I think probably this is is as much as I should say. I'll give you people a change to get back now to the important business at hand, but I do appreciate the opportunity of coming here to speak to you, somewhat randomly and briefly this afternoon. Thank you very much.

Section 1.—Applications in Activation Analysis

ACTIVATION ANALYSIS IN THE CONTEMPORARY WORLD QUESTIONS AND ANSWERS

Plenary Lecture by J. M. A. LENIHAN

Western Regional Hospital Board
Glasgow C.4, Scotland

I. Science and Technology

The purpose of this presentation is to review the characteristics, achievements, limitations and potentialities of activation analysis against the changing background of contemporary science and technology. In particular it is my purpose to consider how the study and practice of activation analysis allows us to contribute to the dialogue between science and technology which is the foundation of the modern world.

Before starting on this task, we should define what is meant by science and by technology. Science is an activity of the intellect, concerned with abstractions such as atoms, forces, fields and currents. It can be practiced—though not for long—with just a pencil and paper or even with no apparatus at all; some of the beginnings of modern science are embodied in Galileo's thought experiments and his technique is widely used today. However, the scientist does not usually make much progress without frequent resort to technology.

Technology is concerned with reality, with concrete things, with the material environment. The prevailing idea that science inspires technology is plausible and sometimes profitable but is, at the best, a half truth and is not a good basis for guiding the activities of mind and hand. The profit arises from the prevailing belief that costly adventures in basic science are justified—and indeed necessary—because useful technology emerges as a bonus.

This is a superficial judgment; the truth is that technology more often inspires science. The process occurs in three distinct but related ways:

1. In a very obvious fashion, technology provides the material support for scientific endeavor. The whole of modern physics rests on the work of Heinrich Geissler, (1814-1870) the German glass blower who was the first to seal metal electrodes into a glass bulb and the inventor of the first satisfactory vacuum pump. The telegraph industry of the last century

contributed greatly to the advancement of electrical science by providing a cheap supply of wire, insulators, switches and measuring instruments for the universities. In the same way, industries which are today concerned with electronics, power production, space research and national defence provide, incidental to their main tasks, a wealth of material for basic studies in nuclear science, solid state physics and many other fields of current endeavor.

2. Technology often produces problems for science to solve. The technology of steam power was abundantly successful in the latter part of the 18th century but the scientific foundation for this achievement was lacking; the search for it provided work for many of the ablest intellects of the 19th century and led to the elaboration of the science of thermodynamics, which still supports every branch of science and engineering.

The communications industry provides another example. Marconi was a good technologist but not much of a scientist. Consequently he did not take heed when told, on the best authority, that wireless waves travelled in straight lines, that the earth was curved and that he was wasting his time in trying to send signals across the Atlantic. He just went ahead and succeeded; the ink was hardly dry on his report when scientists, led by Kennelly and Heaviside, came round to explain why the impossible had happened. In these instances, and many others, technology provided the inspiration by constructing problems of fundamental importance and great intellectual difficulty. The third way in which technology inspires science is more subtle.

3. Science proceeds by questions and answers—or, to describe the same activity in a different way—by making models and checking them against reality. The models that science makes are the reflections of contemporary technology. Thirty years ago the brain was often compared to a telephone exchange. Ten years ago the model was an electronic computer. More recently it has been suggested that the brain is really a holographic device for the storage and retrieval of information.

Today's technology is so richly varied that we may consider several models simultaneously, without waiting for progress to produce fresh ideas. The universe may be regarded as a system of particles interacting according to the laws of dynamics, or as a complex pattern of gravitational, magnetic, electric and nuclear fields—or even as the almost lifeless ashes of the primordial cosmic cataclysm.

Three centuries ago it was fashionable to try to explain the workings of the human body in terms of levers, pulleys, and other technological novelties. Today we can make more sophisticated models. The body might for example be considered as a thermodynamic system, concerned with the transformation and condensation of energy, or as a system of hydraulic and pneumatic circuits, controlled by electrochemical impulses, or as a symposium of feedback loops, servo networks and other cybernetic manifestations.

For the present gathering, where we shall be considering the universe, the more accessible environment and the microscopic and nuclear realms, chemical models are relevant. Here we start from the proposition that function depends on structure and ultimately on composition. In other words the universe, the human body and any other system that we choose to investigate is made of atoms. Techniques for revealing and exploiting the properties of atoms will help us to understand the organization and purpose of the system. It is at this stage that the distinctive characteristics of activation analysis first reveal themselves.

The traditional methods of chemical analysis—and many of the more recently developed techniques—are based on the study of electronic behavior. The electrons occupy the outer parts of atoms and are rather amenable to detachment, transfer or rearrangement to suit the requirements of the experimenter. Optical and x-ray spectroscopy, colorimetry, atomic absorption and electrochemical techniques are examples of methods depending primarily on the behavior of electrons in the atoms under study. Mass spectrometry and nuclear magnetic resonance are among the few analytical techniques which invoke the properties of the nucleus. Activation analysis belongs to this category. The versatility and sensitivity of the technique are associated with the fact that it exploits a very wide range of nuclear properties, making good use of methods and instruments available through advances in other regions of the nuclear realm.

II. What is Activation Analysis?

It is difficult—and perhaps not really necessary—to give a definition of activation analysis. If pressed, however, we might suggest that activation analysis is the revelation of chemical composition through the modification of nuclear behavior. This description includes most of the techniques practiced by activation analysts—and one or two which they have not yet claimed.

At the present time, we do not know very much about the properties of the nucleus, despite the expenditure of great effort during the last 70 years. In these circumstances, our methods of modifying nuclear behavior are rather rough and are in fact based on the technique of hitting with a suitable projectile and watching to see what happens. We would not expect to learn much about the laws of acoustics by throwing a piano out of a window or to improve our understanding of mechanics by striking a watch with a hammer—but experimental methods of comparable crudity have proved remarkably fruitful in nuclear science.

The projectiles that we use fall into three categories—neutrons, photons and charged particles.

A. Neutrons, Fast and Slow

A neutron, having no electric charge, is able to pass rather freely through the outer parts of an atom in order to reach the nucleus. Thermal neutrons (so-called because of their average energy is the same as that of the atoms or molecules of the medium through which they travel) are most often used, for two reasons: (1) The probability of useful interaction with the target nucleus (usually expressed as a cross section) is, in general, greater for thermal neutrons than for any other projectiles. (2) Neutrons are not expensive. Thermal neutrons are readily obtained in great quantities and at little cost. In many countries, a specimen can be placed inside a nuclear reactor and exposed to a constant stream of thermal neutrons at a cost of roughly one cent for 10^{16} neutrons passing through the sample—regardless of how many may be captured by nuclei of the target substance. It is unfortunately not possible to obtain thermal neutron sources of adequate output for general use in the laboratory or factory, though isotopic neutron sources have been used effectively in certain industrial applications. The necessity of bringing the sample to the reactor is of course sometimes a significant inconvenience.

Fast neutrons, at energies of about 14 MeV, are available from the (d,t) reaction, usually achieved by bombarding a tritium—containing target with deuterium ions. The Van de Graaff generator provides a convenient means of achieving this reaction, but more portable devices, some using sealed discharge tubes for the (d,t) reaction, are increasingly used; needing no pumps and only modest power supplies, they have the advantage of compactness and mobility.

The flux of fast neutrons obtainable from an accelerator or discharge tube source is generally well below that of the thermal neutron flux available in a nuclear reactor; indeed the fast neutron flux (at energies up to a few MeV) inside a thermal reactor is as large as that available from many fast neutron generators. The ingenuity required to make effective use of these fast neutrons, in the presence of a great excess of thermal neutrons, has been developed in a number of laboratories.

A typical 14 MeV generator, currently available at moderate cost, will deliver a total output of 10^{11}n/sec, with a useful flux (measured in $n \cdot cm^2 \cdot sec^{-1}$) which may be a hundred or a thousand times smaller. The output from such a machine costs about one cent for 10^{11} neutrons.

Neutrons of intermediate energies, usually between 1 and 8 MeV, may be obtained by using protons or other accelerated particles from a cyclotron to bombard a suitable target. A linear accelerator offers further possibilities for fast neutron production.

Fast neutrons are, in general, useful for short irradiations, partly because of their relatively high cost and also because of the difficulty of maintaining a steady flux from any type of accelerator source. Fortunately, a large number of suitable reactions are available, including some applicable to the light elements (Z less than 10) where thermal neutron sensitivities are very low.

In general, the neutron is an attractive projectile for activation analysis, because its incorporation increases the binding energy of the target nucleus by 6-8 MeV (in addition to the kinetic energy of the neutron) giving scope for a considerable variety of subsequent nuclear rearrangements.

B. PHOTONS

Nuclear behavior can often be altered in a detectable way by bombardment with gamma-ray photons. Most reactions of this kind have an energy threshold and it is generally found best to use photons of 15-25 MeV, available only from a fairly powerful linear accelerator. Cross sections for photon-induced reactions are, in general, 10 to 100 times less than for excitation by neutrons. However, fluxes of 10^{11} or 10^{12} p/sec are obtainable without undue difficulty, allowing the detection of many elements with acceptable sensitivity.

C. CHARGED PARTICLES

Charged particles such as protons, deuterons and ions of hydrogen-3 (tritons) or helium-3 (helions) have a number of important uses, despite the inherent problems associated with limited flux and limited penetration, leading to considerable local heating in the target. Charged particle activation analysis is, in general, applicable only to light elements but can, for certain target elements and certain matrices, achieve sensitivity, specificity or freedom from interference not easily obtained by other means.

III. Activation Processes

In considering the possible outcome of the bombardment of a target, we may consider four processes: (1) transfer of energy (2) incorporation of projectile into target (3) adjustment of compound nucleus and (4) decay of radioactive product.

A. TRANSFER OF ENERGY

Transfer of energy may occur in two ways.

1. Elastic Scattering

Elastic scattering involves some retardation of the neutron with a corresponding gain in kinetic energy of the struck nucleus which is, however, not excited and therefore does not emit any gamma radiation. Elastic scattering may be detected because many of the neutrons are deflected and leave the scene in directions out of the main beam; the transmission loss consequently includes a component attributable to elastic scattering.

2. Inelastic Scattering

Inelastic scattering is a rather different process. The bombarding particles lose some of their energy in the approach to and retreat from the target nuclei. This energy appears as gamma-ray quanta, characteristic of the nuclei involved. The emission of these photons is virtually instantaneous and it is therefore necessary to detect them while the bombardment is still in progress.

B. Incorporation of Projectile into Target Nucleus; Compound Nucleus

The interaction between a neutron (or other projectile) and the target nucleus often proceeds to the point of incorporation, producing a compound nucleus. The rate of incorporation of neutrons into target nuclei may be inferred by the die-away technique. The average lifetime of a thermal neutron in vacuo is several minutes. In a solid medium, the average life is usually measured in μsec.

The rate at which an initial pulse of neutrons dies away depends on the rate at which neutrons are captured in the medium. The attenuation of the original neutron flux will be greater, for example, in a material containing atoms such as sodium and chlorine, with large capture cross sections, than in a material consisting entirely of elements such as carbon, hydrogen and oxygen.

C. Adjustment of Compound Nucleus

The compound nucleus formed by the incorporation of a projectile will not normally be in a stable state but will often release energy, as gamma radiation, in order to attain a more acceptable configuration. The capture gamma radiation (sometimes known as prompt gamma radiation) generated in this way displays an energy spectrum characteristic of the nuclei which have been excited and may therefore be used as a means of identification.

Prompt Emission. Irradiation of a typical specimen will usually give a very complex spectrum of prompt gamma radiation. with energies extending to 6 or 7 MeV and many closely spaced lines. The technique is however quite sensitive: the superior energy resolution of solid state detectors may therefore be exploited without the necessity for inconveniently large neutron fluxes.

The prompt emission does not always consist of gamma radiation. If. for example. activation is achieved by a (p,n) process, the prompt emission will be in the form of neutrons. The energy spectrum of prompt neutrons may be determined by sell-established time-of-flight techniques, with little interference from prompt gamma radiation or other emissions resulting from activation.

This technique has been used in the analysis of gas mixtures [1.2] and has been ingeniously exploited to reveal both the concentration and the depth distribution of carbon. nitrogen and oxygen present as impurities in steel [3].

Because of the Coulomb barrier. the (d,n) reaction. with neutrons of about 3 MeV energy. activates light elements but not the major constituents of the steel sample. Use of monoenergetic deuteron beams (from a Van de Graaff generator) allows the possibility of estimating the depth distribution of the impurities—because the energy of a prompt neutron depends on the energy (and therefore the penetration) of the deuteron which excites the target nucleus.

D. Decay of Radioactive Product

When the compound nucleus has achieved the initial adjustment by emission of prompt gamma-ray or other radiation. the product may be a stable nucleus with little further analytical significance. Very often. however. the nucleus left after prompt gamma-ray emission is still unstable though in the more restrained way characteristic of artificial radioactivity.

The induced radioactivity decays in a typical case with emission of beta and gamma rays having energy spectra characteristic of the nucleus which is involved. Beta radiation may be assayed with excellent sensitivity by geiger counting—a technique which has been somewhat overshadowed by technical developments in gamma-ray measurement but is still important in activation analysis.

Gamma radiation from a radioactive nuclide is generally studied by scintillation counting and spectral resolution with a pulse height analyzer. It is sometimes convenient to detect the emitted gamma-ray radiation by indirect methods—for example. by allowing the radiation to fall on a beryllium target and studying the neutrons emitted in the reaction

$^{11}B(\gamma,n)^{10}B$. This reaction is possible only with radiation of fairly high energy, since it has a threshold of approximately 1.7 MeV

IV. The Environment

Turning now to the scope and applications of activation analysis, we may begin by asserting that the applications are all related to the study of the nature of the environment and of man's interaction with it. This is, of course, a definition which would serve just as well for many other branches of knowledge, but we can concentrate it somewhat by restricting our attention to the following six aspects of the environment: (1) Cosmic, (2) Geological, (3) Biological, (4) Internal biological, (5) Artificial, and (6) Social.

A. THE COSMIC ENVIRONMENT

Study of the cosmic environment is important because the crucial test of any theory seeking to explain the processes by which the chemical elements have been formed is the success with which it can predict the observed abundance of the different nuclear species. As the models become more sophisticated, the need for reliable information on abundance data becomes more pressing. Reliable data for many of the commoner elements in the sun and stars are available from spectroscopic tests but chemical analysis of one sort or another is necessary to determine the composition of meteorites, which represent the only samples of matter from the remoter parts of the universe that we are ever likely to obtain.

The problem is complicated by the grossly uneven distribution of the elements in the universe. Those of low mass number are usually found at high concentrations, presenting no serious analytical difficulty, but most of the chemical elements occur at concentrations of only a few parts per million or even less.

In these circumstances the conventional methods of chemical analysis are not satisfactory. A stony meteorite is a most unattractive specimen for the familiar wet chemical techniques of the analytical laboratory. To apply these methods it is necessary to dissolve the meteorite in acid mixtures or in molten sodium peroxide and it is virtually impossible to avoid contamination with some of the minor elements subsequently to be estimated.

It is here that one of the distinctive features of activation analysis may be demonstrated. When once a sample has been exposed to neutrons or other bombarding particles, the possibility of contamination is virtually eliminated. If, for example, we are trying to measure the indium content of a meteorite, the effect of thermal neutron irradiation is to make some of the indium atoms in the sample radioactive; it is with these atoms that the subsequent analytical determinations are concerned. By being made radioactive, these indium atoms have been set apart from all others of the same nuclear species. No amount of stable indium (in the reagents applied to the irradiated sample or in the containers and other parts of its immediate environment) can contaminate it in a manner detrimental to the accuracy of the final analysis.

Another important advantage of activation analysis is that it distinguishes between the different isotopes of an element. Though many of the common chemical and physical properties of an element (depending as they do on the behavior of the extra-nuclear electrons) are little different as between one isotope and another, the nuclear properties, such as those elicited by neutron activation, are generally very much different. The cosmologist is often interested in the abundance of individual isotopes, as a guide to his speculations on possible methods of nuclear synthesis, or in the relative abundance of different isotopes of an element — sometimes the basis for estimation of the age of a specimen.

During the last ten years, our knowledge of the abundance of the elements in meteorites has been transformed by vigorous application of activation analysis. The main effort was originally concerned with the study of minor constituents. For many of these elements, the abundances have been revised — always in a downward direction — by factors of 10 or even 100 in relation to previously accepted results. More recently, activation analysis has been applied to the estimation of more abundant elements such as silicon and oxygen.

Activation Analysis of the Lunar Surface. The composition of the moon has long been a matter of interest to astronomers, geologists and cosmologists. Substantial experimental facilities have been assembled for the study of rock and soil samples returned after the manned landings expected in the near future. Plans have been made also for analytical studies *in situ* — partly because instrumental landings will be more easily and more often achieved than manned landings, partly because of the danger of contamination or chemical change as the samples move from the vacuum of the lunar atmosphere to the oxygen-rich terrestrial environment and partly as an aid to the geological mapping of the lunar surface or the selection of samples for more detailed examination after return to earth.

The main requirements for activation analysis of the lunar surface *in situ* are: (1) a source of bombarding particles or radiation, (2) a detecting system with pulse height analysis. Of the elements most likely to be found on the moon, silicon, aluminum, iron and oxygen can be estimated satisfactorily by activation analysis with 14 MeV neutrons. Magnesium, sodium and potassium are best studied by thermal neutron activation analysis.

For simplicity of design and limitation of weight it would be desirable to have the source and the detector close together. In this event, however, it would be impossible to avoid activation of the sodium iodide crystal in the detector. An alternative design puts the source and the detector at opposite ends of a column which can be rotated electrically, about its midpoint, between activation and assay [4].

Problems associated with neutron activation of the lunar surface are being vigorously studied in several laboratories. Meanwhile the first chemical analysis of the moon has been made [5] by activation analysis using alpha particles from a source of curium-242; the energy spectrum of the back-scattered alpha particles and of the protons obtained from (α,p) reactions both give useful information about major constituents of the lunar surface; the main conclusion so far reached is that the sample analyzed by equipment flown in the Surveyor V landing in September 1967 was rather similar in composition to a terrestrial basalt.

B. THE GEOLOGICAL ENVIRONMENT

The study of terrestrial rocks is not in general complicated by the analytical problems mentioned in the preceding section. Meteoritic material is usually available only in small samples and its elemental composition is important because, for example, concentrations of trace or minor constituents may provide a useful framework for the classification schemes. Terrestrial rocks, on the other hand, are available in great abundance and have been extensively analyzed by generations of geochemists.

In these circumstances, the scope for activation analysis is rather limited. It is true that many of the earlier estimates of rock composition are inaccurate, particularly in relation to trace elements—but the geologist, having so much information of other kinds to excite and reassure him, does not rely very heavily on the results of chemical analysis.

1. Oil Prospecting

Though activation analysts have so far contributed little to the intellectual foundations of geology, they have substantial opportunities in the application of geological knowledge and ideas to problems of economic importance.

Some of the most interesting technical developments of recent years are associated with the oil industry. Oil is a mixture of hydrocarbons, consisting by definition of carbon and hydrogen. It is fortunate that neither of these two elements is very suitable for activation analysis by fast or thermal neutrons, since in these circumstances other materials present as impurities may be detected without interference from the matrix.

Many of the undesirable impurities, including sodium, vanadium, manganese, iron and nickel are present at levels in the range 1-1000 ppm and are readily detected by activation analysis. The presence of vanadium is particularly significant, since this element poisons the costly platinum catalysts used in the cracking process to transform the crude oil into more valuable products.

Activation analysis has been little used in surface prospecting for solid minerals—except occasionally in the search for silver—but finds an important place in the battery of techniques used by the oil prospector.

The method often used in the search for oil and other minerals is to drill a bore hole and to examine the immediate surroundings, often at considerable depth, by whatever analytical techniques can be exploited. Straightforward activation analysis can be used in mineral bore holes to indicate the presence of a number of metals. Aluminum, manganese and copper may be detected by thermal neutron activation, using a polonium-beryllium source. Silicon may be detected by a fast neutron reaction $^{28}Si(n,p)^{28}Al$. Isotopic sources of thermal neutrons can, by indicating the presence of sodium and chlorine, allow identification of interfaces between oil and salt water.

In general, however, neutron activation analysis in the difficult conditions prescribed by the limits of a bore hole is not very sensitive, either for constituents of the oil itself or for other materials which, by their presence, may give clues to the location of oil deposits.

2. Die-away Techniques

More sophisticated techniques are, however, being appreciated and exploited to an increasing extent [6]. The scope of these developments may be illustrated by considering the sequence of events when a burst of 14 MeV neutrons is emitted from a generator sunk in a bore hole and the thermal neutron population at a place near the source is subsequently measured by a suitable detector.

Fast neutrons from the generator will lose energy in two ways. Firstly they may undergo elastic collision with nuclei in the immediate environment. In an elastic collision, the neutron loses energy which appears as kinetic energy of the struck nucleus; there is however no nuclear excitation. Hydrogen nuclei are the most effective in this slowing down process. Consequently the time taken by the fast neutrons in reaching thermal energies—that is, the time required for the thermal neutron population around the detector to reach a maximum—gives an indication of the hydrogen content of the material in the immediate vicinity.

The thermal neutron population immediately starts to decline, because of capture in the surrounding nuclei. The slope of the die-away curve may be used to obtain an indication of the concentration of sodium chloride in the vicinity, since sodium and chlorine are usually the only elements with large thermal neutron capture cross sections which are likely to be encountered at significant concentrations in a bore hole. The die-away curve will not distinguish between oil and fresh water but the method can be used for example to locate the interface between oil and salt water.

The capture of a thermal neutron is characterized by the instantaneous emission of capture gamma-ray radiation. This radiation, like the thermal neutron flux, dies away over a period of several hundred microseconds. The decay curves, are however, not the same in the two processes because, for example, the capture gamma-rays have a greater range than thermal neutrons. Consequently the neutron die-away rate is largely dependent on the composition of the contents and lining of the bore hole, whereas the decay rate of the capture gamma-ray radiation is influenced by material further out from the bore hole.

Nuclei which have captured thermal neutrons often become radioactive and emit activation gamma rays over a period of time thereafter. This radiation is unlikely to be detected by the experimental arrangements envisaged in the preceding paragraphs, unless the corresponding activity has a half life of less than a few milliseconds.

The original fast neutrons from the generator may lose energy by the process of inelastic collision, which has not so far been considered. In this process, the energy lost by the neutron is used to raise the struck nucleus to a higher energy level, from which it immediately descends by emission of gamma-ray radiation. This gamma-ray radiation may be detected during the fast neutron pulse, before thermalization has occurred to any substantial extent.

In an interesting experiment made under simulated (but very realistic) conditions, [7] the initial pulse of fast neutrons lasted for 15-20 microseconds. A gamma-ray detecting system operated during the first 15 microseconds of the pulse responded to inelastically scattered gamma-ray radiation from carbon and oxygen. The detector was then switched off for 10 microseconds. During the next counting period, beginning 25 microseconds after the beginning of the original pulse, hydrogen, silicon and chlorine were detected by capture gamma-ray radiation.

Similar techniques have been used in oil fields with useful results; the oil content of a deposit can be inferred from the carbon/oxygen ratio and clues to the nature of the surrounding rocks from the presence of silicon (indicating sandstone) and magnesium, indicating dolomites [8].

C. The Biological Environment

In approaching the biological environment, we meet many of the problems already familiar from the cosmological and geological context. To begin with the raw material is essentially the same; living matter represents a transient rearrangement of the atoms constituting the more permanent cosmic and geological surroundings. Consequently the wide variation in elemental abundance which is characteristic of the geosphere is observed also in the biosphere with certain important differences in detail, arising because the creation and maintenance of living matter requires the selective concentration from the environment of a number of elements such as carbon, oxygen, calcium and sulphur at the expense of other elements including hydrogen, helium and silicon.

Significant for the activation analyst however is the general pattern with a few elements present in concentrations of several per cent, others in the parts per million or parts per billion range and quite a lot for which no reliable data yet exist.

Gross elemental abundances are less interesting to the biologist than to the cosmologist. The separation of the chemical elements into the groupings now found in living matter is, at the present state of knowledge, not of such basic interest as the processes of nuclear synthesis occurring in the stars.

Interferences. The activation analyst does however meet many familiar problems. Often the element in which he is interested occurs in the presence of a great many others, equally apt for the induction of radioactivity and all contributing to a confused pattern of signals when the stage of resolution, interpretation and quantitative numerical assessment is reached.

Faced with this problem, we can seek relief in various ways.

1. The element in question may be separated from its neighbors before irradiation. This is in general a hazardous process, since it brings the inevitable danger of contamination, but has been successfully accomplished in certain circumstances.
2. The activity induced in the element which is being studied may be separated by chemical means after irradiation. This is, on the whole, a simple, quick and very reliable technique and is usually necessary if the ultimate sensitivity of activation analysis is to be reached.
3. The induced activity may be separated from the interfering signals which accompany it by resolution of the gamma-ray spectrum. At the present time, scintillation detectors give good sensitivity but poor resolution, while solid state detectors give excellent resolution at lower sensitivity. There is, however, little doubt that the progress of technology will lead to solid state detectors or other devices combining the desirable attributes of good sensitivity with good energy resolution.

4. Naturally enough, the activation analyst chooses his weapons carefully before starting his attack. Though thermal neutron activation remains the most widely applicable technique, rapid progress has been made in recent years with the development of photoneutron activation (using the (γ,n) reaction), with fast neutron activation (both with 14 MeV particles and with the output from cyclotrons and other accelerators) and in the development of charged particle activation analysis techniques.

In any particular situation, the analyst must judge which method of activation will give a significant modification in the nuclear behavior of the species which interests him, without activating other elements in the sample or in the matrix to an inconvenient extent. By choice of bombarding projectiles and by exploiting thresholds and resonances it is now possible to find activation analysis techniques applicable to almost all of the elements and to a very wide variety of practical situations. This judgment does not, however, justify an attitude of complacency or relaxed satisfaction; on the contrary it indicates that many of the truly formidable problems for the activation analyst have, in the absence of suitable techniques, not yet been formulated.

Other aspects of man's place in – and relations with – the biosphere will be considered later, in relation to the social environment.

D. The Internal Biological Environment

Studies of gross chemical composition on the intact organism are generally of limited interest since it is difficult to relate information gained in this way to the complex of physiological processes which are the ultimate object of experimental study. There are, however, some important situations in which information about the gross chemical composition of an entire organism or, more often, a limited part of it, is of genuine scientific or clinical significance but is inaccessible to the normal methods of chemical analysis or radioactive tracer tests.

1. In Vivo Studies

Activation analysis *in vivo,* for the study of body composition in the intact human subject, represents an exciting and fruitful area of research with considerable promise for the future. The experimenter is, of course, restrained by the reflection that his patient or experimental subject is not so robust as a lump of rock. A typical specimen irradiated in a nuclear reactor may be exposed to a radiation dose of millions of rems without serious damage.

Only the least sensitive of living creatures, such as microorganisms, will withstand an insult of this kind; for the more highly organized examples of biological creation—where activation analysis and other bold experimental techniques are especially necessary or relevant—the sensitivity to radiation is even greater. The experimenter in this area requires patience, skill and self-discipline of a high order—the more so because there are no regulations or other official guidance to help in judging the scientific or clinical benefits of the technique alongside the radiation hazards.

2. *Fast Neutron Irradiation*

In vivo activation analysis of the human subject began in 1964 when Anderson and his colleagues [9] estimated total body sodium in two normal subjects after whole body exposure to 14 MeV neutrons. Partial moderation was obtained by a polyethylene blanket and some of the remaining fast neutrons were reduced to thermal energies in their passage through the tissues of the body.

An important problem for *in vivo* activation analysis arises because thermal neutrons, which are more likely to cause effective activation in the tissues, are heavily absorbed; for this reason it is impossible by any practicable combination of thermal neutron fields to achieve uniform irradiation in the body or even in a relatively small portion of it.

Fast neutrons have ample power of penetration and, for many elements, the cross sections for nuclear activation are quite adequate; unfortunately the radiation dose associated with a given flux of fast neutrons is many times greater than the corresponding dose for thermal neutrons.

Despite these difficulties it is possible to induce measurable amounts of radioactivity in a human subject after whole body irradiation corresponding to a dose of less than one rem. Anderson *et al* used fast neutron doses of about 0.1 rad, equivalent to one rem, from a 14 MeV neutron generator.

After neutron irradiation, the subjects were transferred to a whole body counter for assay of the induced radioactivity. The nuclides most conspicuously observed were ^{24}Na and ^{38}Cl. More recently, Chamberlain *et al* [10] irradiated a number of cadavers and normal subjects with neutrons (in the energy range 0.1 to 8 MeV) obtained from a lithium target bombarded with protons from a 60 in. cyclotron. Achieving a rather rapid transfer of the irradiated subjects from the cyclotron chamber to a whole body counter, Chamberlain and his colleagues were able to detect ^{49}Ca, a nuclide of half life approximately 9 minutes obtained by thermal neutron capture in ^{48}Ca. Radiation doses incurred in these experiments were about 1.5 rem.

Cyclotron-produced neutrons have been used also by Palmer *et al* [11] with a radiation dose which they estimated at 0.38 rem. They suggest that it should be possible to measure sodium, chlorine, and calcium with reasonable precision by thermal neutron activation, nitrogen and phosphorus by fast neutron activation using the reactions $^{14}N(n,2n)^{13}N$ and $^{31}P(n,\alpha)^{28}Al$, hydrogen by detection of capture gamma rays in the reaction $^{1}H(n,\gamma)^{2}H$ and carbon by photoneutron activation in the reaction $^{12}C(\gamma,n)^{11}C$.

Table 1. Activation analysis in vivo: possible reactions.

	Half life of product
$^{23}Na(n,\gamma)^{24}Na$	15 h
$^{37}Cl(n,\gamma)^{38}Cl$	37 m
$^{1}H(n,\gamma)^{2}H$	prompt
$^{48}Ca(n,\gamma)^{49}Ca$	9 m
$^{31}P(n,\alpha)^{28}Al$	2.3 m
$^{14}N(n,2n)^{13}N$	10 m
$^{12}C(\gamma,n)^{11}C$	20 m
$^{16}O(n,p)^{16}N$	7 s

3. Standardization

A major difficulty in estimating the total body content of an element by activation analysis is the problem of standardization. For *in vitro* studies, a standard (containing a known amount of the element under investigation, in a pure form) is irradiated alongside the experimental sample and is then subjected to the same radiochemical or instrumental procedures for assay of induced radioactivity.

If thermal neutron irradiation is achieved in a reactor, nonuniformity of flux throughout the sample (which is usually of quite small dimensions) is not a serious considerations, nor is it usually necessary to consider the possibility of any difference in the neutron fluxes to which the sample and the standard are exposed.

Standardization is rather more difficult with fast neutrons or with charged particles, where the region of uniform flux is usually quite small and where the flux cannot always be held constant during the time needed for an irradiation.

When the object under irradiation is an entire human body, the problem of standardization is formidable. Ideally, we should like to achieve a uniform flux of neutrons throughout the body and to make the assay of induced radioactivity in a whole body counter geometrically arranged so that its response is independent of the position of the radioactive material being measured.

The second of these conditions can be approached more closely than the first. For an element uniformly distributed throughout the body, standardization with a phantom (for example, a polyethylene mannikin filled with an appropriate solution) would be enough. Of the elements so far studied, sodium comes nearest to fulfilling this specification. Though the concentration of this element is about twice as great in bone as in other tissues of the body, reasonable confidence might be placed in the result of *in vivo* activation analysis.

4. Total and Exchangeable Sodium

The two attempts so far made to estimate total body sodium by activation analysis have however given discordant results. Anderson *et al* [9] estimated total body sodium (adjusted to 70 kg subject) at about 75 g. Using the same experimental subjects they found virtually the same figure for exchangeable sodium—that is, the content of the body pool of sodium measured by an isotope dilution technique 24 hours after the injection of a tracer dose of sodium-24. Chamberlain *et al* [12] found total body sodium to be 80 g and exchangeable sodium to be 66 g.

Further studies are necessary to resolve this discrepancy and to decide whether part of the sodium in the body is indeed isolated from the possibility of equilibration with an injected tracer dose. About one third of the sodium content of the body occurs in bone and there is some evidence to suggest that about half of this fraction is not exchangeable; when bone biopsies were taken after administration of sodium-22, the specific activity of sodium in bone was no more than half of that in plasma, even after 28 days [13].

5. Calcium

For calcium, which is very unevenly distributed throughout the body, there is no possibility of making an adequate phantom for standardization and it is therefore all the more important to seek uniform neutron irradiation. Assuming that the experimental subject is irradiated first in the prone and then in the supine position, uniformity of neutron flux throughout the body depends mainly on the distance from the cyclotron target. This consideration underlines the necessity for a high output cyclotron; because of the short half life of calcium-49, it is not possible to compensate by using a longer irradiation time. It is of course also desirable to have a very sensitive whole body counter.

6. Thyroid Iodine Estimation

Opportunities and problems of a different kind arise in relation to activation analysis of limited regions of the body. The estimation of total thyroid iodine by *in vivo* activation analysis, first suggested in 1965, has been pursued [14] in a way which avoids some of the difficulties and uncertainties mentioned in the preceding paragraphs.

Iodine-129, administered two weeks before the neutron irradiation, lodges in the thyroid gland in much the same way as any other iodine tracer; since this isotope emits low energy photons, the amount present in the gland at any time may be estimated with reasonable accuracy by external counting. This exercise is facilitated if the iodine-129 is itself exposed to a small dose of thermal neutrons before being ingested, so as to produce a little iodine-130 which has a convenient half life of about 12 hours and gives more penetrating gamma-ray radiation.

When once deposited in the thyroid, the iodine-129 acts as a flux monitor for the subsequent *in vivo* neutron irradiation, allowing the thyroidal iodine-127 to be estimated from the relative counting rates attributable, after neutron irradiation of the gland, to iodine-128 and iodine-130 (or its short-lived companion iodine-130m).

The use of iodine-129 as an internal standard in this way has the advantage that inhomogeneity of neutron flux during irradiation is of no concern; the technique just described measures the specific activity iodine-127/iodine-129. Assuming only that the iodine-129 is, on a macroscopic scale, distributed through the gland in the same way as the indigenous iodine-127, it is not necessary to achieve uniform neutron flux throughout the thyroid or even to irradiate the whole of the gland. This method has so far been used cautiously in sheep but its extension to human subjects is in progress.

Activation analysis of body tissues *in vivo* is often complicated by the great preponderance of sodium and the corresponding abundance of sodium-24 after irradiation. In this connection, the estimation of thyroid iodine is facilitated (1) by the remarkable concentration of this element in the gland and (2) by the fortunate circumstance that iodine is trapped in the thyroid whereas sodium and chlorine, which may be activated along with iodine, are rapidly removed by the circulation.

Activation analysis by the study of capture gamma-ray radiation has been demonstrated in the living subject by Comar *et al* [15]. They irradiated the tibia with thermal neutrons and obtained conspicuous peaks corresponding to calcium and chlorine in the spectrum of capture gamma-ray radiation; no other elements were detected.

7. *Future of In Vivo Activation Analysis*

There are many intriguing possibilities for the future development of *in vivo* activation analysis. Estimation of total body concentrations of particular elements is unlikely to be accurately achieved until effective methods of standardization can be devised. The construction of a realistic phantom is seldom practicable and the crude approach involving chemical analysis of cadavers presents formidable technical and ethical problems.

Though the development of internal standards represents the most attractive way out of these difficulties, no obvious lines of enquiry are apparent in this connection at the present time. Limited progress may be expected through the availability of more powerful neutron generators (and more sensitive detecting systems).

Because of the paramount need to reduce the radiation dose incurred by the experimental subject, the more favorable conditions associated with the study of short-lived activities should be exploited. There are for example interesting possibilities in the use of pulsed neutron sources and sophisticated counting equipment to study isomeric states (produced by neutron or gamma-ray irradiation) with half lives in the msec or μsec region. Cross sections for such reactions are often agreeably large, allowing adequate sensitivity with small radiation doses.

There is need for authoritative guidance on the ethical problem associated with *in vivo* activation analysis of the human subject. Existing regulations and recommendations framed to deal with diagnostic radiology and occupational radiation exposure, are not adequate or appropriate in this connection. National and international regulatory agencies have so far been unwilling to commit themselves. There is a danger that the technique may become discredited through enthusiasm untempered by wisdom and caution.

8. *Trace Elements*

In vivo studies on human subjects are restricted to major body constituents such as calcium and sodium or (as in the thyroid investigations already mentioned) to elements showing an unusual degree of concentration or immobility in a particular region of the body. *In vitro* studies allow the range of elements – and of problems – to be considerably enlarged.

Sometimes the imagination of the experimenter will contrive useful and important applications out of modest resources. A diagnostic test proposed for cystic fibrosis depends on the elevated sodium level in nail clippings. Activation analysis may provide a simple way of achieving this test on a large scale at little expense. The simplicity and sensitivity of activation analysis have been exploited also in studying clinical problems related to zinc, manganese and a few other elements.

Difficult and intriguing problems appear when the less abundant constituents of the body are brought under review. In entering the realm of knowledge, we immediately encounter the mystique associated with the trace elements. It is not difficult to see why this group of elements have been set apart from the rest. Firstly, they occur in such small amounts as to make measurement and scientific or clinical study difficult or impossible. This situation is however being modified through the application of activation analysis and a few other modern analytical techniques.

Secondly, the trace elements are clearly different in behavior from the 12 bulk elements (Table 2) which have recognizable tasks in maintaining the structural integrity or biochemical efficiency of the body.

Table 2. Bulk elements.

	Amount in 70 kg man
Oxygen	45500 g
Carbon	12600
Hydrogen	7000
Nitrogen	2100
Calcium	1050
Phosphorus	700
Sulfur	175
Potassium	140
Sodium	105
Chlorine	105
Magnesium	35
Iron	4

For the few trace elements which have had substantial study, the remarkable contrast between minute concentrations and spectacular biological effects can often be explained by reference to catalysis in enzyme systems, allowing the same atoms to be used repeatedly.

But some of the less familiar elements, whose biochemical purpose is still obscure, provide temptation to scientists and clinicians seeking hypotheses to illuminate the natural history of disease. Many of these speculations are no longer immune from verification or rebuttal by precise experiment and it is in this area that some of the most significant tasks await the activation analyst.

The magnitude of the task is evident when we consider that, apart from the 12 bulk elements already noted, only seven others are known with certainty to be essential for the nutrition of man (Table 3). Many of the remaining 70 or so elements occur regularly in the tissues of the body and it is to be expected some of them (perhaps including vanadium, zirconium and chromium) will before long be recognized as essential.

Table 3. Essential elements.

Date of recognition	Element	Amount in 70 kg man
1939	Zinc	2300 mg
1928	Copper	150
1930	Iodine	30
1919	Manganese	20
1956	Molybdenum	5
1948	Cobalt	3
1959	Selenium	?

Careful studies of trace element concentration in various tissues will often suggest novel lines of investigation, not all of which will turn out to be fruitful. It is known, for example, that many elements, including cadmium, tin, and fluorine, accumulate in the human body, or in particular tissues, with advancing age. These changes may be of biological significance but are more probably explicable in terms of ingestion from the environment.

Other elements, including copper and chromium, are rather abundant in the newborn but their concentration decreases with increasing age. It is tempting to construct hypotheses explaining these curious effects, but necessary to remember that humdrum explanations may fit the facts better. The concentration of copper in the liver of a newborn infant is five or ten times greater than in an adult liver. The significance of this difference becomes apparent with the realization that milk contains very little copper. The infant's enhanced store of this element satisfies metabolic needs until he is old enough to take a more varied diet. The activation analyst can cross interdisciplinary boundaries rather freely but must keep his eyes open; many interesting answers are lying around unrecognized because the correct questions have never been asked.

9. Essential or Fortuitous?

The recognition of an essential trace element by the established methods of physiology and biochemistry is a long and complicated process. For some elements, present at very low concentrations, convincing proof of the effects of deficiency is difficult to obtain because it is virtually impossible to construct a diet containing a sufficiently minute amount of the element concerned.

Activation analysis, if pushed to the limit of sensitivity, can certainly help in the attack on this problem. A significant task—familiar in the present surroundings—is the preparation of ultra-pure reference materials—not only as an analytical standards but as dietary constituents.

Activation analysis can help the search for new essential elements in a different way. If an element has a regular biochemical or physiological role in the body, departure from the optimum concentration level is likely to produce recognizable effects. If, on the other hand, an element is a mere fortuitous inclusion, the amount present in the body may vary more widely without the evocation of regulatory mechanisms.

Thus, the amount of sodium in blood will seldom vary by as much as 10% from the normal level of 2 mg per ml, but the concentration of arsenic in hair will often be less than half or more than twice the median value of about 0.5 ppm.

The variability of trace element content, expressed as the standard deviation of (log concentration) in a population of samples from normal people, may provide an index of the extent to which an element is essential [16].

10. Clinical Studies

Though any studies aimed at illuminating the dark recesses of the periodic table are to be welcomed, it is too soon to expect many therapeutically useful correlations between individual trace elements and particular diseases. More realistic, though often tedious and unspectacular, is the effort to gather reliable data about the occurrence and metabolism of trace elements in various tissues, organs and systems of the body. Several important investigations of this kind in recent years have demonstrated differences in trace element composition between normal and malignant tissues or have suggested correlations of other kinds between trace elements and disease. The relevance of such observations is however not likely to be fully apparent until we have achieved a better scientific appreciation of the biochemical and physiological significance of the trace elements.

In providing the basic data for these advances, activation analysis has an important but not an exclusive role. In many laboratories, atomic absorption or other modern techniques of analysis would rightly be regarded as more appropriate than activation analysis, because staff, equipment and experience are all readily available without conspicuous additional expenditure of effort or money; these advantages are often enough to outweigh modest differences in sensitivity or precision.

11. Stable Tracers and Activation Analysis

There are however areas of clinical research in which the peculiar advantages of activation analysis are of considerable importance. The scope of radioactive tracer investigations is quite often limited because the element which it is desired to investigate does not have isotopes with suitable properties. The half life of the only available isotope may be too short to follow the physiological process under investigation; alternatively the biological half life of the only available isotope may be so long that the patient receives an unduly large radiation dose. Sometimes, as in children and pregnant women, the use of radioactive tracers is discouraged by regulatory agencies and on other occasions, for example when working with large animals, a hazardous amount of radioactive material must be used in order to achieve labeling of the organism at an adequate specific activity for the experiment.

In these circumstances, it is often advantageous to use stable isotopes as tracers, to be detected subsequently by activation analysis, thereby avoiding all radiation hazard to the experimental subject and the bystanders. Successful work of this kind requires (1) the existence of a relevant element in a stable isotopic form which, though rare in the natural state, can be artificially enriched (for example by electromagnetic separation) to a relatively high percentage concentration and (2) a suitable nuclear reaction for the estimation of this particular isotope by activation analysis. Fortunately, these conditions are quite often satisfied, though the technique of stable tracer activation analysis has not yet been fully exploited [17,18].

E. THE ARTIFICIAL ENVIRONMENT

The object of all industrial manufacturing operations is the modification, in response to human needs or desires, of materials taken from the environment. It is therefore not surprising that some of the general considerations regarding the scope and exploitation of activation analysis, developed in the preceding pages, are relevant in the industrial context also. Since a large proportion of the world's analytical chemists are employed in industry, and since the mere survival of an industry indicates its ability to produce an acceptable product, it might be thought that only marginal improvements could be achieved by refinement of analytical techniques. It is true that in the keenly competitive industrial atmosphere, activation analysis will be subjected to sharper critical assessment than in some of the other areas of knowledge already reviewed, where intellectual curiosity may predominate over economic realism. There are nevertheless many analytical problems in industry for which activation analysis is to be preferred because it is more rapid, more accurate or more convenient; sometimes the alternative methods are so inadequate as to be little used.

The industrial uses of activation analysis may conveniently be divided into (1) laboratory determinations and (2) on-line determinations.

1. Oxygen in Steel

The steel maker adds oxygen to molten iron in order to remove impurities but must impose a careful control on the proportion of oxygen which appears in the final product, where it can significantly alter the metallurgical properties of the finished steel. Activation analysis systems now available commercially for the measurement of oxygen in steel or other metals use a simple 100-200 kV generator of the Cockcroft-Walton type to drive a sealed tube neutron generator based on the familiar (d,t) reaction, with an output of about 10^{11} neutrons/sec.

Pneumatic transfer systems position the sample first in the neutron beam (typically for 30 sec) and then in the counting position close to a scintillation detector, commonly for a further 30 sec. The reaction used is $^{16}O(n,p)^{16}N$. The product nuclide emits gamma-rays at 6.1 and 7.1 MeV which are rather easily detected. Through continued improvements in the irradiation, handling and detection systems, fast neutron activation analysis is now fully competitive with other techniques for the estimation of oxygen in metals, giving the advantages of rapidity and reliability.

2. Nitrogen in Food

Estimation of nitrogen is a reliable method for determining the protein content of many food-stuffs. The Kjeldahl technique traditionally used for nitrogen estimation is firmly established but the needs of the modern food processing industry have encouraged the search for quicker and easier methods.

The reaction $^{14}N(n,2n)^{13}N$ is, at first glance, not very attractive. ^{13}N decays by positron emission with a 10 minute half life; the resulting annihilation gamma-rays of energy 0.51 MeV are readily detected—but radiation of the same energy rises from the reaction $^{31}P(n,2n)^{30}P$. A correction can be applied for this interference, but not for the error introduced by the presence of carbon and hydrogen in the sample. Protons displaced by neutron bombardment engage in the reaction $^{13}C(p,n)^{13}N$, giving additional counts which are of course indistinguishable from those attributable to the (n,2n) reaction on ^{14}N.

This interference increases the apparent nitrogen content of the sample by several ppm; consequently the accurate estimation of nitrogen is possible only at levels of 0.5% or more. Fortunately the grain products to be examined usually contain 3–10% of nitrogen.

Equipment which was commercially available in 1967 was able to estimate nitrogen in grain products with a guaranteed reproducibility of 1% (slightly better than is generally claimed for the Kjeldahl process) and at a total cost of $1.80/sample, which is about 50% more than for a Kjeldahl estimation. It is however expected that the cost of routine nitrogen estimations by activation analysis will fall before long to about $0.60/sample.

3. On-line Analysis

Though activation analysis is often regarded as a technique for the estimation of elements present at low concentrations in small samples, it offers significant possibilities also for rapid analysis of materials in bulk [19].

Work of this kind is best done with fast neutrons, since no other particles appropriate for activation analysis are available from compact and relatively inexpensive sources. The good penetrating power of fast neutrons, and of the gamma-ray radiation associated with the induced radioactivity, make it possible to use large samples. In this way, the sampling errors which can be troublesome in many industrial materials are greatly reduced. An additional advantage is gained because, since the detecting equipment responds, broadly speaking, to the total amount of radioactivity presented to it, a smaller neutron flux will suffice to produce adequate activity in a large sample.

Another advantage which becomes apparent in these circumstances related to the problem of standardization. When a small sample, and its accompanying standard, are irradiated by fast neutrons from a generator delivering the maximum flux of which it is capable, temporal and spatial irregularities in the neutron flux make it necessary to rotate the specimen and standard (sometimes about two perpendicular axes simultaneously) in order to reduce the effects of flux variation. When however the neutron output demanded is only 10^8 or 10^9 neutrons/sec, stabilization is very much easier and the neutron flux at the sample position can be kept constant to within 2% over a period of many hours.

On-line applications of activation analysis are concerned with major or minor constituents of the material under investigation, but not with trace constituents. Fast neutron activation analysis is particularly suitable for the detection of light elements. This facility complements the resources provided by x-ray fluorescence techniques, which are more sensitive for the heavy elements.

The abundance of fast neutron reactions among the light elements is often an embarrassment to the analyst. The (n,2n) reaction will usually yield a positron emitter, detected by the characteristic annihilation radiation at 0.51 MeV. Radiation of the same energy will however be released in the annihilation of electron-positron pairs resulting from the absorption of high energy gamma-ray radiation associated with quite different activities induced in the sample.

Further problems arise because the impact of fast neutrons on hydrogen present in the analytical specimen releases protons which, as has already been noted, can generate confusion and interference by engaging in their own nuclear reactions. There is however ample evidence that these difficulties can be overcome by the ingenuity of the nuclear technologist.

Equipment now in production or at the prototype stage allows the determination of many elements in raw materials or finished products or at intermediate stages in processing. The enterprise used in this work is illustrated by an analytical system developed for the examination of coal.

Fast neutrons from a portable generator irradiate coal as it passes on a conveyor belt. Carbon and oxygen are estimated by the study of gamma-ray radiation associated with the inelastic scattering process, using scintillation detectors close to the point of irradiation. Aluminum and silicon are estimated by the assay of induced radioactivity, using separate scintillation detecting equipment about 15 ft downstream. The total ash

Table 4. On–line activation analysis: typical examples.

Element to be estimated	Suitable reaction	Half life of product
Carbon in coal	$^{12}C(n,n')^{12}C$ (inelastic scattering)	–
Nitrogen in grain	$^{14}N(n,2n)^{13}N$	10 m
Oxygen in coal	$^{16}O(n,n')^{16}O$ (inelastic scattering)	–
Fluorine in fluorite	$^{19}F(n,\alpha)^{16}N$	7.4 s
Sodium : phosphorus in detergent	$^{23}Na(n,\alpha)^{20}F$	12 s
	$^{31}P(n,\alpha)^{28}Al$	2.3 m
Silicon in iron ore or coal	$^{28}Si(n,p)^{28}Al$	2.3 m
Aluminum in coal	$^{27}Al(n,p)^{27}Mg$	
Copper in copper ore	$^{63}Cu(n,2n)^{62}Cu$	9.7 m
Barium in barytes	$^{138}Ba(n,2n)^{137m}Ba$	2.6 m

content of the coal can be estimated from the silicon and aluminum content, the calorific value from the carbon content and the moisture content from the amount of oxygen in the sample. Some applications of on-line activation analysis are noted in Table 4.

F. The Social Environment

The justification for the practice of science and technology is that these activities, when properly guided and exploited, can make life more purposeful, more satisfying and more enjoyable—not only for the practitioner but for mankind in general. The short and exciting history of activation analysis, happily free of that arrogance which (masquerading as intellectual curiosity) can be seen in quite a few areas of contemporary science and medicine, has demonstrated welcome concern for the improvement of the social environment.

In looking around the world today it is hard to escape the conclusion that progress is not uniformly beneficial. The most obvious effect of technological progress is that the rich nations become richer while the poor become poorer. The gap between crime and the law grows wider because criminals are more enterprising in using the many resources provided by technology. Contamination of the environment proceeds apace because the community lacks the means (or the will) to balance the benefits of cheaper food, better transportation and profitable industrial activity against possible damage to health, amenity and ecological equilibrium. Activation analysts have significant opportunities in this situation.

Forensic Science. Except for the occasional red-handed capture, the identification of a criminal is possible only by studying his interaction with the immediate environment at the scene of the crime. The range of techniques available to the forensic examiner includes some (such as the study of fingerprints and bloodstains) which are highly successful, but there are many notable gaps; a few of them are being filled by activation analysis.

In attempting a comparison between two samples of hair (obtained, for example, from the scene of a crime and from the head of a suspect) the forensic expert has until recently been obliged to rely on physical methods of examination; chemical analysis by conventional techniques is impossible, because a single hair is much too small a sample. Activation analysis of single hairs allows the estimation, by nondestructive methods, of at least a dozen elements; if instrumental assay of the induced radioactivity is reinforced by radiochemical separation (which of course destroys the hair) many more elements may be determined.

Here, as always when a new experimental method arrives, it is important that enthusiasm for the technique does not outrun the practical realities of the situation in which its application is sought. Chemical analysis of a hair, however detailed and accurate, does not tell the whole story unless the following factors are also taken into account:

1. The metabolic activity (and consequently the chemical composition) of a single hair changes, in a way which is not yet fully cataloged, during the growth cycle which may last for 20 months or more.

2. Since the hair is a convenient pathway for the excretion of many metallic elements, the trace element composition of a single hair is significantly affected by variations in dietary intake.

In these circumstances, the chemical analysis of hair does not provide a uniquely characteristic signature such as a fingerprint. Since however the trace element profile of a hair will often display peculiarities attributable to diet, occupation or environment and sufficiently pronounced to outweigh the uncertainties mentioned in the preceding paragraph, it is quite often possible to use activation analysis as the basis of an opinion which, though not decisive, may nevertheless be of considerable value to the court.

As Guinn has observed [20], activation analysis is the most powerful method yet developed for the comparison of human head hair specimens as to the probability of common origin.

V. Paint and Glass

Activation analysis of inanimate material can be of considerable value for forensic purposes. Small fragments of paint sometimes constitute significant evidence in cases of house breaking or in crimes involving motor vehicles. Though the major constituents of a particular type of paint show little variation (except when the manufacturing process is radically altered) the minor constituents occur irregularly and often show considerable differences between one batch and another. Similarly, paint of the same general specification from different manufacturers will be very similar in the concentrations of major constituents but will show wide variations in respect to trace element composition. These differences arise, naturally enough, because the minor elements, contributing nothing to the color, consistency or covering power of the paint, are in no way controlled by the manufacturer. Comparison of paint samples by activation analysis is now a reliable technique for forensic purposes; studies of other materials, including plastics, rubber, lubricants and paper are in progress. Glass is a more difficult material in this respect, since—in most countries—the number of independent manufactures is very small; in Britain, most of the flat glass, providing for all except specialized needs, comes from a single manufacturer. In these circumstances, the trace element composition may give a clue to the date when a sample of glass was made, but variations between one batch and another of the same age are likely to be rather small.

A. ART AND ARCHAELOGY

An interesting opportunity for activation analysis—sometimes not so remote from the criminal realm as it might seem—relates to the attribution of paintings.

The major constituents of white lead, a basic material used by painters for more than five centuries, do not become appreciably radioactive under neutron bombardment, but several minor constituents—really impurities—including Cu, Zn, Br, Ag and Sb are rather easily activated. By measuring the concentrations of these elements, which are related to changes in manufacturing technique, it is often possible to fix the date of the painting—or rather the date when the pigment was made.

Direct activation analysis of an entire painting is also useful [21]. The activity induced by exposure to a thermal neutron flux of $10^9 \text{n} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$ for 20 minutes, assayed by gamma-ray spectroscopy and autoradiography, contains a considerable amount of information about the artist's materials and technique.

Archaeologists have long recognized the significance of chemical composition as a guide to the origin and classification of objects in metal, glass or pottery. Ancient glass was first analyzed by Klaproth as long ago as 1798. In recent times, systematic analysis has been made by destructive techniques such as emission spectrography and atomic absorption as well as by nondestructive methods including x-ray fluorescence and x-ray diffraction.

Often the archaeologist's interest relates to minor constituents rather than to trace elements. In these circumstances, the extreme sensitivity of activation analysis is not needed, but the possibility of simultaneous determination of several elements without damage to the specimen is often important.

Here as in other fields, activation analysis is not always the most informative method of study. In examining the composition of glass, x-ray diffraction has an outstanding advantage. Since glass is amorphous, x-ray diffraction can reveal a crystalline constituent (commonly the opacifying agent) without matrix interference—and, what is often of great value, reveals the molecular composition rather than the atomic composition.

B. ENVIRONMENTAL CONTAMINATION

Contamination of the environment is one of the significant hazards of affluence. Pollution which is gross enough to offend the senses is easily identified and the analytical chemist does not have decisive role in the attack. There are, however, more subtle forms of pollution which may, in the long term, do more damage than the obvious insults to sight and smell.

Deliberate or inadvertent modification of the environment is a problem of increasing importance. It is true that man has always been surrounded by the waste products of domestic and communal activity—but the nature of the rubbish is now changing significantly.

When we discard a bone or a tin can we return it to a familiar environment, from which it was assembled and into which it can be absorbed by relatively quick and straightforward processes.

But when we discard a plastic bag or when we spray crops with chemicals remote in composition and effects from any found in nature, we are severely taxing the biological scavenging mechanism. After a very long time, the chemical and microbiological make-up of the biosphere will become adapted to the new needs—but in the interval we cannot be sure that the discarded materials will be denatured before returning to food cycles. In these circumstances, it is important to study the biological consequences of chemical modifications to the environment.

For many minor elements, including some for which no biochemical function has yet been elucidated, the human body maintains good homeostatic control, fluctuations of intake from diet or from other contacts with the environment being compensated by variations in excretion rate.

For other elements, rather wide variations in body burden appear to be consistent with normal health. It is, however, difficult to reach confident conclusions as to the toxic effects of a particular element on the basis of individual clinical histories.

It is not certain that the threshold for biological damage coincides with the level of intake or body burden corresponding to serious illness. Harmful effects may well occur at lower levels of internal contamination but are not at present recognized, because they are indistinguishable by any simple clinical test from the minor fluctuations superimposed on a state of good health—however that elusive concept may be defined. These fluctuations may be random statistical artefacts or may be transient changes related to the body's defensive action against disturbances which never reach clinical maturity.

A realistic assessment of the hazard presented by the release of a particular toxic element into the environment cannot be obtained by studying the small number of individuals who, through idiosyncracy or abnormal exposure to the hazard, demonstrate obvious signs of poisoning. A more satisfactory approach would use the techniques of epidemiology, originally developed for the study of infectious diseases but now successfully used in relation to non-transmissable afflictions.

The effects of exposure to a supposedly toxic element can best be revealed by studying two groups of people, one with little or no exposure and one with more substantial exposure. Correlation should be sought between morbidity statistics (collected if necessary over a period of years) and personal exposure to the toxic element in question.

This exposure can, for many elements, best be assessed by activation analysis of hair and nail samples. Examination of blood and urine is clearly impracticable if adequately large and representative communities are to be involved in the study. On the other hand activation analysis of hair and nail is a socially acceptable procedure, involving no discomfort, inconvenience or embarrassment to the subjects and having the additional advantage that samples can be gathered at leisure, for analysis at a convenient time and place which may be remote from the scene of the investigation.

Work of this kind, both among the general public in selected localities and among the more specialized at-risk groups to be found in many industries, represents an important opportunity to tackle a significant and growing hazard, but has not so far commended itself to those responsible for the preservation of the public health on a global or a national scale.

VI. Conclusion

This brief tale has been offered as a pointer rather than as a map. The varied and challenging opportunities presented by activation analysis can hardly be reviewed in a lecture—or even in a conference. They reach far into space and time, illuminating the basic problems of cosmology—but are useful also in the microscopic realm, helping our understanding of vital processes in cells and tissues.

In the broader sense, activation analysis encourages us to learn more about the world around us—as it was, as we have made or changed it and as it may become. By sharpening our appreciation of the interdependence of man and his environment, the practice of activation analysis demonstrates the fruitful union of science and technology, of intellectual curiosity and social responsibility.

VII. References

[1] Peisach, M., and Pretorius, R., Chem. Commun., 632 (1966).

[2] Naude, W. J., Peisach, M., Pretorius, R., and Strebel, P. J., J. Radioanal. Chem. **1**, 231 (1968).

[3] Moller, E., Nilsson, L., and Starfelt, N., Nucl. Instr. and Meth. **50**, 270 (1967).

[4] Hislop, J. E., and Wainerdi, R. E., Anal. Chem. **39**, 28A, (1967).

[5] Turkevich, A. L., Franzgrote, E. J., and Patterson, J. H., Science, **158**, 635 (1967).

[6] Clayton, C. G., United Kingdom Atomic Energy Authority, Research Group Report, AERE—R5368 (1967).

[7] Tittman, J., and Nelligan, W. B., J. Petr. Tech. **12**, 63 (1960).

[8] Hoyer, W. A., and Rumble, R. C., J. Petr. Tech. **17**, 801 (1965).

[9] Anderson, J., Osborn, S. B., Tomlinson, R. W. S., Newton, D., Rundo, J., Salmon, L., and Smith, J. W., Lancet, **ii,** 1201 (1964).

[10] Chamberlain, M. J., Fremlin, J. H., Peters, D. K., and Philip, H., Brit. med. J. **2,** 581 (1968).

[11] Palmer, H. E., Nelp, W. B., Murano, R., and Rich, C., Phys. Med. Biol. **13,** 269 (1968).

[12] Chamberlain, M. J., Fremlin, J. H., Peters, D. K., and Philip, H., Brit. med. J. **2,** 583 (1968).

[13] Edelman, I. S., James, A. H., Baden, H., and Moore, F. D., J. clin. Invest. **33,** 122 (1954).

[14] Lenihan, J. M. A., Comar, D., Kellershohn, C., and Riviere, R., J. Nuc. Med. **9,** 110-115 (1968).

[15] Comar, D., Riviere, R., Raynaud, C., and Kellersohn, C., Radioaktive Isotope in Klinik und Forschung, Bd VIII, Urban r Schwarzenberg, Munich (in press).

[16] Lenihan, J. M. A., and Smith, H., in Nuclear Activation Techniques in the Life Sciences, I.A.E.A., Vienna, 1967, pp. 601-614.

[17] Guinn, V. P., in Isotopes in Experimental Pharmacology, L. J. Roth, Ed., Chicago University Press, 1965, pp. 23-32.

[18] Bethard, W. F., Schmitt, R. A., Olehy, D. A., Kaplan, S. A., Ling, S. M., Smith, R. H., and Dalle Molle, E., in Nuclear Activation Techniques in the Life Sciences, I.A.E.A., Vienna, 1967, pp. 533-544.

[19] Rhodes, J. R., ORO-2980-17 (1967).

[20] Guinn, V. P., in Proceedings of the First International Conference on Forensic Activation Analysis, V. P. Guinn, Ed., Gulf General Atomic, Inc., San Diego, California, 1967, p. 29.

[21] Sayre, E. V., *ibid.,* pp. 119-132.

CHAPTER 1

APPLICATIONS TO THE ENVIRONMENTAL SCIENCES

Synopsis of Discussions

GEORGE W. LEDDICOTTE, *Chairman*

University of Missouri
Columbia, Missouri

Man's first campfire and his early primitive living conditions began to rapidly change his almost virgin environment. His population explosions and scientific and technical achievements have continuously increased these environmental changes. As a result, the accumulation of human and animal wastes, industrial wastes, atomic debris, and wastes resulting from Nature's own deliberate changes of the terrestrial, aquatic and atmospheric environments have brought man to the realization that he must have a better understanding of how these changes affect his well-being.

A session like this is unique in that it points up the facts that we must constantly think about the pollutants in our environments in terms of what they are and what we need to do to control them in order to achieve a better environment. The papers in this section were a mere beginning of understanding the importance of how one analytical methodology *i.e.*, activation analysis, might be used to support the research interests of environmental scientists.

One of these reports, Brar *et al,* was concerned with natural and pollution sources of chlorine, bromine, and iodine. The extensive sampling of air over inland United States regions added to the information about the distribution of these elements in the particulate and gaseous phases of the atmosphere. The data presented showed evidence of the chemical reactivity that affected the variations in the chemical composition of stable aerosols. The authors concluded that iodine is not a significant air pollution source associated with urbanization and industrialization of these inland areas. They also concluded that the bromine concentrations in these areas arose predominantly from natural sources. It has also been suggested that the high chlorine concentrations observed, could have resulted from both local pollution sources and natural chlorine aerosol levels.

In another paper, Loucks *et al,* we had the report of a team of scientists from the USPHS, the Pollution Control Department of the City of Chicago and the Argonne National Laboratory on the results obtained in an investigation concerned with the introduction of trace elements into the atmosphere from the burning of fuels and refuse. At least 12 different trace elements were detected in the air over metropolitan Chicago. As the authors pointed out, a large scale sampling and analysis effort is required in order to determine whether these pollutants are hazardous to the inhabitants in this urban area.

A report, Dudey *et al,* was also given on the detection and the determination of the concentrations of stable elements in over-ocean environments. The authors considered that it was important to understand the source of these marine aerosols and the mechanisms of their transport over oceanic areas so that geochemical knowledge could be increased and the problems of possible pollution control of such species as Sb and Cd could be defined.

Houtman emphasized the use of activation analysis to understand the transport of sand and fine-grain material sediments through the delta systems of the Rhine, Ems, and Chao Phya Rivers. This investigation has resulted in the conclusion that the rapid mobility of trace elements (such as Mn, Sm, La, Zn, As, Sc, Cr and Co) takes place as organometallic complexes. The authors also conclude that the ultimate concentration of trace elements in arable soils will depend on the composition of river solids and on the mobility of an element during the various stages of soil genesis. As a result, these processes and conditions could lead to trace element concentrations which are marginal for plant growth and health.

Stable tracers and activation analysis have been used, Cappadona, to study the movements of solid substances in water in order to resolve the kinetics of erosion on seacoasts, the migration of sand or gravel along litorals, and to understand the influence of sand and slime on navigable channels of river estuaries and canals. Stable tracers of Ag and Co were mixed with sand and scattered throughout these areas and then samples collected and analyzed. The preliminary data obtained afford a possibility to carry out more complete research programs to obtain more precise data for use by hydrologists in their studies on the movements of sand and slimes in these areas.

Similarly, a preliminary report by Channell on the use of stable rare earth elements in estuary water tracing was made. The paper described the initial developments resulting from this investigation. Such parameters as the choice of tracers, their natural background concentrations, the introduction of the tracers into the suspended solids and muds of the San Francisco estuary system, and the potential influences of the suspended biological and inorganic materials in the estuarine water system upon the analytical method are being studied. The results of these studies are expected to provide a systematic plan for studying this estuary region. In another paper by Guinn, a report has been made on the use of an instrumental method of activation analysis to determine the origin of marine fuel oils in harbor areas. The characterization of these oils by their trace element contents should provide a practical means of identification of the source of oil pollution of waters that should aid in the enforcement of present oil pollution laws.

Water control research concerned with the determination of trace vanadium in supply waters was reported in another paper by Linstedt. A simple activation analysis method has been developed to determine the low concentrations of vanadium in water in order to study its possible physiological significance. A report by Leddicotte was also given on the significance of the use of activation analysis in determining a variety of trace element species for research interests in ecology, medicine and pollution control. Each of these interesting areas are very much aware of the importance of a specific and sensitive analytical method like activation analysis to assist them in their trace substance research.

Generally, all of these papers provided useful information about experimental techniques and equipment. They all have emphasized the need for more exacting sample collection procedures, and conclusions were fostered to the idea that in many instances preconcentration procedures might be employed to bring about more conclusive results. Furthermore, it was anticipated that many samples would have to be collected and analyzed in any of these projects in order to provide accurate data for any environmental science evaluation on pollution.

If it is possible to predict on the future utilization of activation analysis for problems in environmental science, it can be said that the activation analyst will have an important role.

The papers given in this session emphasized that activation analysts have already been given an opportunity to make their contributions simultaneously with those of other scientists in many different disciplines.

THE HALOGEN COMPOSITION OF AEROSOL PARTICLES OVER LAKE MICHIGAN

Ronald H. Loucks, John W. Winchester, Wayne R. Matson
and Mary A. Tiffany

Department of Meteorology & Oceanography
University of Michigan
Ann Arbor, Michigan 48104

I. Introduction

The halogen elements chlorine, bromine, and iodine are distributed in the atmosphere between particulate and gaseous phases and show evidence of chemical reactivity which affects the variation of chemical composition with particle radius in the stable aerosol range of 0.2 to 20 microns. Previously published analyses of naturally-occurring aerosols for halogens are restricted almost entirely to samples collected in coastal locations of the U.S. where local sources of sea salt are present [1-4]. In this investigation we are undertaking the first extensive sampling in the inland U.S. in regions where both natural and pollution sources of the halogens may be important. The results are to be compared with earlier studies of both naturally-occurring aerosols and aerosols containing lead of pollution origin [5-7].

High sensitivity means of chemical analysis are employed in order to permit sampling of cubic meter volumes of air which can be fractionated into particles of different sizes and permit sampling times of a few hours or less. The halogens are determined by neutron activation [8], and lead and certain other trace metals are determined using anodic stripping voltammetry [9,10]. Particle size sorting is accomplished using cascade impactors of six or more stages with polyethylene impaction surfaces suitable for activation analysis and for trace metal removal using ultrasonic vibration.

II. Experimental

As the principal objective of the sampling program, a field location was selected which would not have local sources of halogens, lead, and other trace metals of interest but with well-defined pollution sources at some distance removed as well as a regional natural distribution of these elements in the atmosphere. Sampling above the surface of Lake Michigan from the deck of the research vessel Inland Seas operated by the University of Michigan was viewed as affording detection of air pollutants emanating from coastal locations, in particular the Chicago-Gary urban and industrial complex when winds were from the south, or the determination of the natural background of these elements, especially when the winds were from the north. During May 1968, a cruise was carried out where samples of aerosol particles were collected during two daylight traverses between Grand Haven, Michigan, and Chicago, Illinois, and during a continuous 24 hour sampling period overnight in the middle of the southern basin of Lake Michigan. During this time the winds varied from northerly to southerly.

Aerosol sampling was carried out using a Scientific Advances six-stage cascade impactor and an Andersen sampler, both devices resolving particles into groups differing by about a factor of two in radius in the stable aerosol range. Impaction on the surfaces of polyethylene inserts was judged to be efficient in the moist atmosphere over the lake. Possible contamination from the ship smoke-stack was monitored by Hi-Vol filter samplers operating in various places on the ship, and by the degree of darkening of some of the filters the impactor locations were selected so as to be free of contamination.

Chemical analysis for halogens was carried out by neutron activation of the polyethylene inserts, washing, and separation of I, Br, and Cl using solvent extraction followed by beta counting. Analysis for Pb, Cd, and Cu was performed by anodic stripping voltammetry using a composite mercury graphite electrode. Polyethylene inserts used in the Andersen sampler were cut into two portions, one for neutron activation and one for anodic stripping, the latter processed by desorbing the trace metal deposit into high purity aqueous NaCl solution using ultrasonic vibration. The sensitivity of both methods of analysis is adequate to determine these elements in all but the cleanest air using a few cubic meters of air volume passed through the impactor stages in several hours or less.

The locations and circumstances of the individual runs are given in Figure 1 and Table 1. Runs 8 and 9 were taken in the middle of the southern basin of Lake Michigan and runs 3 and 4 while the ship was at rest in a harbor of South Chicago, an urban and industrial location a few kilometers inland from the lake shore. The other samples were taken while the ship was underway over the stretches of water and during the times indicated.

III. Results and Discussion

A summary of the halogen results is given in Tables 2, 3, and 4. In all cases the six Scientific Advances cascade impactor stages and the backup filter were analyzed individually for 7 separate data points per sampling

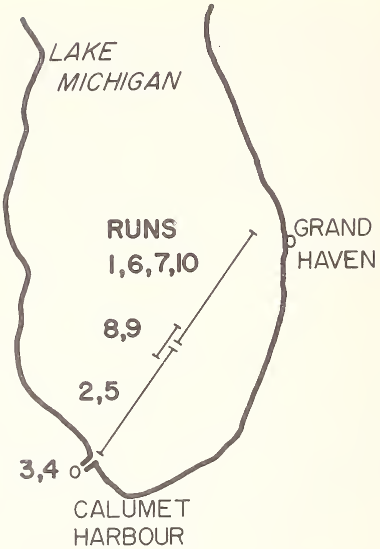

Figure 1. The ship's routes during the sampling runs.

Table 1. Circumstances of the runs.

Run[a]	Date, 1968	Time, EST	Wind, m/s	R.H., %	Clouds
1	May 20	0722–1156	NW @ 5	85	4/8
2	May 20	1225–1606	NW @ 5	80	4/8
3	May 20–21	1652–0224	NNW @ 5	75	0
4	May 21	0307–0559	W @ 5	95	0
5	May 21	0640–1102	SW @ 3	85	1/8
6	May 21	1124–1450	SW @ 3	85	1/8
7	May 22	0633–1033	SSE @ 3	98	7/8
8	May 22	1102–1912	SSE @ 2	80	fog
9	May 22–23	1940–0614	var. @ 3	98	8/8, rain
10	May 23	0650–0952	ENE @ 4	100	8/8

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[a] For locations see Figure 1 and text.

run. Because of lack of space only a summary of these data is presented in the tables. The data for lead are not yet available at this writing.

Two major observations should be made in scanning the data for iodine in Table 2. (1) A large fraction of the iodine is held by particles of radius less than 0.25 micron without apparent systematic differences due to location, winds, or relative humidity. (2) The total iodine concentration does not vary with proximity to the Chicago-Gary urban-industrial area or with winds which could carry pollutants from that area to the sampling location, and the total iodine concentrations observed compare favorably with those observed in Hawaii and in polluted as well as unpolluted

Table 2. Iodine concentrations.

Run	Total concentration ng/m^3	Percent of total with radius <0.25 μm
1	7.4 ± 0.7	70
2	1.0 ± 0.4	65
3	7.3 ± 0.4	52
4	1.9 ± 0.5	37
5	<0.7	>90
6	5.0 ± 0.6	64
7	1.0 ± 0.4	>90
8	1.9 ± 0.4	32
9	0.9 ± 0.2	44
10	0.7 ± 0.3	>90
Mean:	3 ± 1	
Fairbanks background:	3.0 ± 0.3[a]	
Fairbanks pollution:	3.9 ± 0.3[a]	
Hawaii background:	≥ 1.7[b]	

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[a] Means of 10 rural samples and 20 city samples collected by Millipore filter in and around Fairbanks, Alaska, during winter [6, 7].

[b] Mean of 8 samples collected at the seashore by cascade impactor but without backup filter [4].

locations in Fairbanks, Alaska. Therefore, we do not observe iodine to have signifcant air pollution sources associated with urbanization.

The data for bromine in Table 3 indicate (1) that a large fraction of bromine is contained on particles of radius less than 0.25 micron, and there is no apparent systematic variation of this tendency with location, winds, or relative humidity. However, (2) the bromine values in Calumet Harbor are very much greater than the samples collected over the lake, strongly suggesting an urban pollution origin of much atmospheric bromine. The Fairbanks pollution average is not far from these values. The lake runs showed similar values independent of wind direction, but it should be borne in mind that the wind speeds were very mild during this sampling cruise. The similarity of these values with Fairbanks and Hawaii background values suggests that this bromine concentration is predominantly natural.

Table 3. Bromine concentrations.

Run	Total concentration ng/m^3	Percent of total with radius <0.25 μm	Percent of total with radius <0.5 μm
1	24 ± 3	91	94
2	11 ± 1	50	75
3	1380 ± 90	61	77
4	407 ± 20	29	64
5	22 ± 2	50	89
6	13 ± 2	80	80
7	27 ± 2	56	78
8	42 ± 2	45	68
9	31 ± 2	46	79
10	22 ± 1	51	74

Mean of runs 3 and 4: ~900

Mean of the other runs: 24 ± 4

Fairbanks background: 35 ± 3[a]

Fairbanks pollution: 500 ± 50[a]

Hawaii background: ~11[a]

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[a] See notes to Table 2.

The chlorine data, Table 4, (1) show negligible amounts held by particles smaller than 0.25 micron radius for the samples collected over the lake, and in the majority of cases at least a third of the chlorine is held by particles above 1 micron in radius without apparent correlation with the meteorological parameters of Table 1. (2) The two Calumet Harbor samples contrast by showing not only greatly higher concentrations than any of the other runs but a substantial fraction of chlorine in the smallest particle size fraction. A local pollution source is suggested, and because the concentration is so much greater than observed in the Fairbanks pollution study, we ascribe this tentatively to an industrial source other than automotive or other fuel combustion. (3) The average of lake samples is similar to the Fairbanks area background values, and these concentrations may represent natural chlorine aerosol levels.

Table 4. Chlorine concentrations.

Run	Total concentration $\mu g/m^3$	Percent of total with radius $<0.25\ \mu m$	$<0.5\ \mu m$	$<1\ \mu m$
1	0.26 ± 0.04	<4	6	21
2	0.15 ± 0.02	<6	39	69
3	9.6 ± 1.0	58	83	89
4	12.2 ± 1.6	28	74	85
5	0.21 ± 0.03	<5	64	74
6	0.28 ± 0.03	<4	23	51
7	0.71 ± 0.04	<2	20	48
8	1.11 ± 0.06	<1	10	35
9	0.26 ± 0.02	<4	49	49
10	0.70 ± 0.05	<2	13	68

Mean of runs 3 and 4:	~11
Mean of the other runs:	0.5 ± 0.1
Fairbanks background:	0.5 ± 0.03[a]
Fairbanks pollution:	1.4 ± 0.2[a]
Hawaii background:	~3.6[a]

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[a] See notes to Table 2.

In general, by comparison with the Hawaii and Fairbanks data, the Lake Michigan data suggest that natural concentration levels have been detected in many of the samples. The presumably natural bromine and iodine are carried to a great extent by the smallest size particles, in contrast to chlorine which is on mainly larger size particles. There is no evidence that iodine is a significant air pollutant associated with the urban or industrial areas tested, but both bromine and chlorine show anomalously high concentrations in the urban localities. The atmospheric input of bromine may be largely the result of burning leaded gasoline, but the inputs of chlorine may be from various urban and industrial sources. The question of atmospheric residence times and removal rates must await further sampling and analysis before answering.

IV. Acknowledgments

This work was supported in part by contract AT(11-1)- 1705 with the U.S.A.E.C., grant AP-00585 from the U.S.P.H.S., facilities grant GA-811 from the N.S.F., and a grant from the Phoenix Memorial Fund of the University of Michigan. We are grateful for the use of the University of Michigan ship Inland Seas, and one of us (R.H.L.) is indebted to the Bedford Institute of Oceanography, Nova Scotia, for partial salary support to carry out this work.

V. References

[1] Duce, R. A., Winchester, J. W., and Van Nahl, T. W., J. Geophys. Res. **70,** 1775 (1965).
[2] Duce, R. A., Winchester, J. W., and Van Nahl, T. W., Tellus **18,** 238 (1966).
[3] Winchester, J. W., and Duce, R. A., Tellus **18,** 287 (1966).
[4] Duce, R. A., Woodcock, A. H., and Moyers, J. L., Tellus **19,** 369 (1967).
[5] Lininger, R. L., Duce, R. A., Winchester, J. W., and Matson, W. R., J. Geophys. Res. **71,** 2457 (1966).
[6] Winchester, J. W., Zoller, W. H., Duce, R. A., and Benson, C. S., Atmospheric Environment **1,** 105 (1967).
[7] Winchester, J. W., and Duce, R. A., in Nuclear Activation Techniques in the Life Sciences, I.A.E.A., Vienna, 1967, pp. 631-43.
[8] Duce, R. A., and Winchester, J. W., Radiochim. Acta **4,** 100 (1965).
[9] Matson, W. R., Roe, D. K., and Carritt, D. E., Anal. Chem. **37,** 1594 (1965).
[10] Matson, W. R., and Roe, D. K., Analysis Instrumentation Vol. 4, Plenum Publishing Corp., New York, 1967.

THERMAL NEUTRON ACTIVATION ANALYSIS OF AIRBORNE PARTICULATE MATTER IN CHICAGO METROPOLITAN AREA

S. S. Brar and D. M. Nelson

Radiological Physics Division
Argonne National Laboratory
Argonne, Illinois 60439

E. L. Kanabrocki, C. E. Moore, and C. D. Burnham

Chemistry Department
Loyola University
Chicago, Illinois 60626

D. M. Hattori

City of Chicago
Department of Air Pollution and Control
Chicago, Illinois

I. Introduction

Awareness and concern are increasing that modern industry is adding into our atmosphere and water waste byproducts which may be injurious to health. The U. S. Public Health Service, pollution control departments of large cities, and many other scientific teams are routinely monitoring the air for the presence of "smoke", sulfates, and fallout. The burning of coal, oil, and refuse, in addition to their combustion products, are continuously introducing many trace elements into the atmosphere. At present, no large-scale effort is directed toward their detection, even though they are collected and are available for determination. Therefore, before these pollutants can be judged as hazardous, this information is necessary.

There are many techniques which can be used to perform these measurements. Thermal neutron activation analysis is relatively simple and does not involve the destruction of the sample, especially, if the study is limited to gamma-ray emitting nuclides. Furthermore, computer techniques for multinuclide gamma-ray spectrometry are readily available. And the measurement sensitivity for many induced nuclides is more than adequate, when high flux reactors are used in conjunction with NaI(Tl) crystals.

Dust is commonly collected on a filter by drawing air through a vacuum pump. Consequently, the filter becomes part of the sample. Therefore, for satisfactory analysis of the trace elements present in the air by activation analysis, one needs a filter which is free of high thermal neutron cross section elements. Commonly used asbestos and fiber glass base filters, even though they have high collection efficiency for small particles, are not suitable for thermal neutron activation analysis because they contain large amounts of Na, Cl, and other elements. In this study, we have used a cellulose-base filter paper, furnished *gratis* by Union Carbide Corp. which exhibits a low gamma-ray background after an exposure to thermal neutrons.

II. Experimental

On April 4, 1968, air particulate samples were collected simultaneously at twenty-two different locations throughout the Chicago Metropolitan area. Since the collection efficiency of cellulose-base paper is not known for small particles, two filter papers were used on some samplers, while on others the cellulose-base filter was backed with glass fiber-base filter. Tables 1 and 2 show the weight in grams of the particulates collected on the front and back papers. The analysis of these data shows that front paper retained about 80% of dust by weight when backed with either paper.

Each pump sampled approximately 2000 cubic meters of air through an 18 cm by 23 cm filter paper during a 24 hour period. One centimeter square was cut from each of the exposed filters and heat sealed into thin polyethylene sheet. That is, each sample to be irradiated contains the dust from roughly five cubic meters of air. The heat sealing was done by the use of a Teflon coated soldering iron tip so as to minimize contaminating the sample (For a satisfactory heat seal a reduced line voltage is recommended for the soldering iron).

Since some of the induced nuclides have "short" half lives only two samples at a time were irradiated for a period of one minute in $2.4 \times 10^{13} \mathrm{n \cdot cm^{-2} \cdot sec^{-1}}$ flux of Argonne National Laboratory's CP-5 rabbit facility. Because the neutron flux from one irradiation to the next cannot be assumed to be constant, an accurately weighed Mn standard was used as a flux monitor. Table 3 shows the short-lived gamma-ray nuclides detected, with their half lives and principal gamma-ray lines. Figure 1 shows the gamma-ray spectra for one of the irradiated samples, as derived by the use of a 4 in. × 4 in. NaI(Tl) crystal inside a one inch thick mercury shield. Subsequently, the samples were reirradiated for a period of 24 hours and counted at decay time of one and two months to determine some of the long-lived nuclides.

Table 1. Distribution of 24–hour air particulate matter collected on cellulose and glass fiber filters (23 cm × 18 cm).

Station	Filter Cellulose–top		Glass fiber bottom		Total weight
	g	%	g	%	g
Morton Grove	0.0783	70.73	0.0324	29.27	0.1107
Taft, Chicago	0.0886	75.14	0.0293	24.86	0.1179
Lakeview, "	0.1801	80.11	0.0447	19.89	0.2248
Steinmetz, "	0.0988	80.45	0.0240	19.55	0.1228
GSA	0.2057	74.31	0.0711	25.69	0.2768
Austin, "	0.1402	79.52	0.0361	20.48	0.1763
Kelly, "	0.1406	74.47	0.0482	25.53	0.1888
Lindbloom, "	0.0723	70.88	0.0297	29.12	0.1020
Hyde Park, "	0.2297	88.72	0.0292	11.28	0.2589
CVS, "	0.1188	81.59	0.0268	18.41	0.1456
Fenger, "	0.1072	77.51	0.0311	22.49	0.1383
Carver, "	0.1275	79.58	0.0327	20.42	0.1602
Clay, "	0.1093	77.24	0.0322	22.76	0.1415
Sullivan, "	0.1598	81.65	0.0359	18.35	0.1957
VonStuben, "	0.1299	77.00	0.0388	23.00	0.1687
Average	0.1324	77.92	0.0361	22.07	0.1686
Standard deviation	0.0447	4.59	0.0114	4.59	0.0527
Cooley, Chicago 48 hours	0.5235	87.83	0.0725	12.17	0.5960

Table 2. Distribution of 24–hour air particulate matter collected on cellulose filters (23 cm × 18 cm).

Station	Filter Cellulose–top		Cellulose–bottom		Total weight
	g	%	g	%	g
ANL, (4 cm × 13 cm)	0.0380	73.07	0.0140	26.93	0.0520
Calumet, Chicago	0.1423	81.12	0.0331	18.88	0.1754
Logan Sq., "	0.2695	81.96	0.0593	18.04	0.3288
Hale, "	0.1592	80.73	0.0380	19.27	0.1972
Stevenson, "	0.1272	77.70	0.0365	22.30	0.1637
Average	0.1472	78.92	0.0362	21.08	0.1834
Standard deviation	0.0874	3.64	0.0141	3.64	0.0984
Crane, Chicago	0.4583	89.88	0.0516	10.12	0.5099

Table 3. Some of the "short"–lived nuclides induced in particulate suspension (Chicago Metropolitan Area) after 1 minute irradiation in an approximate 2×10^{13} n · cm^{-2} · sec^{-1} flux.

Isotope	Half life	Principle gamma–ray energies (MeV)		
^{28}Al	2.3 min	1.78		
^{52}V	3.77 min	1.43		
^{37}S	5.04 min	3.10		
^{49}Ca	8.7 min	3.10		
^{80}Br	17.6 min	.62	.511	
^{38}Cl	37 min	1.64	2.15	3.79
^{56}Mn	156 min	.84	1.80	
^{24}Na	900 min	1.38	2.76	

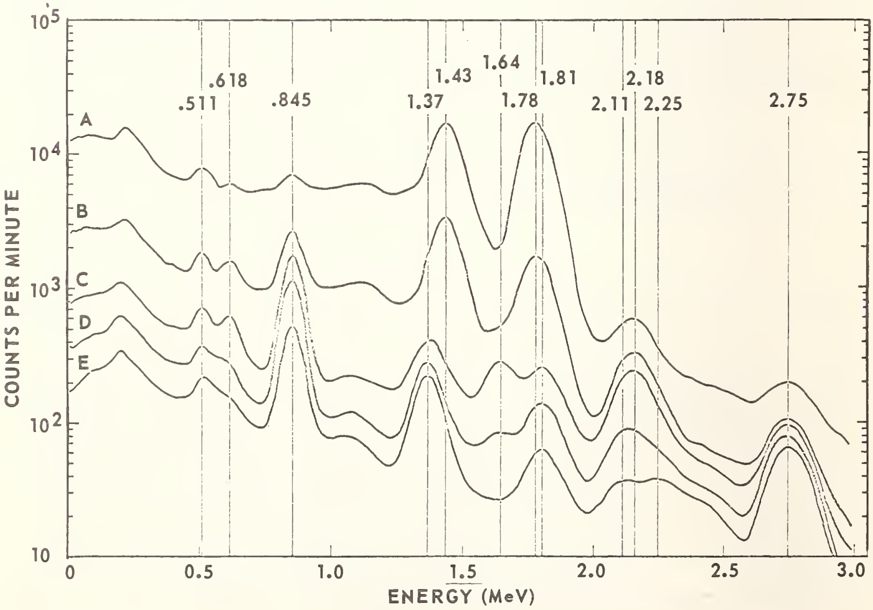

Figure 1. Gamma-ray spectrum of an irradiated sample.

For the quantitative determination of detected elements, accurately weighed standards were prepared and heat sealed in polyethylene. These were then irradiated in the reactor and their spectral shapes determined under conditions of geometry similar to the unknowns. The simultaneous equations method of analysis was employed, and the results were procured on a G.E. 225 computer. Figures 2 to 12 show these results. Tables 4, 5 and 6 give additional data.

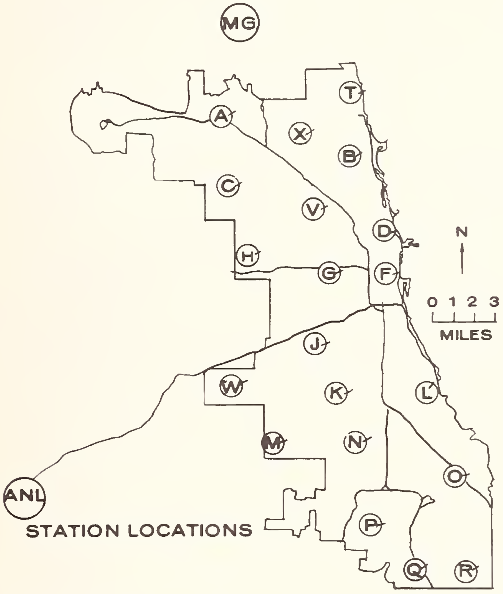

Figure 2. Scattergram of particulate collection stations.

III. Conclusion

A thermal neutron activation analysis in conjunction with NaI(Tl) crystal and gamma-ray spectrometry has been used to detect 13 trace elements present in Chicago Metropolitan surface air, and this number may be increased if a Ge(Li) detector is employed. The sensitivity of the system is such that the method can be used for routine measurements if dust is collected onto a "clean" filter.

IV. Acknowledgment

This work in part was supported by the U. S. Atomic Energy Commission and the U. S. Public Health Service. Some of the preliminary results were presented to the Seventh Annual Meeting (Chicago, Illinois) of the Society for Applied Spectroscopy in May 1968.

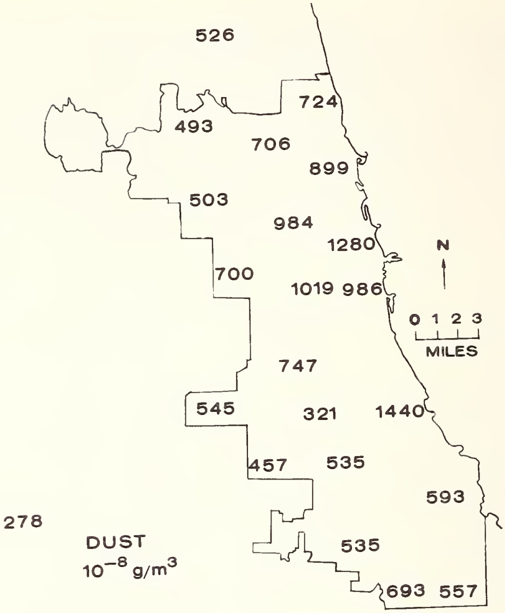

Figure 3. Scattergram of dust levels observed in the air.

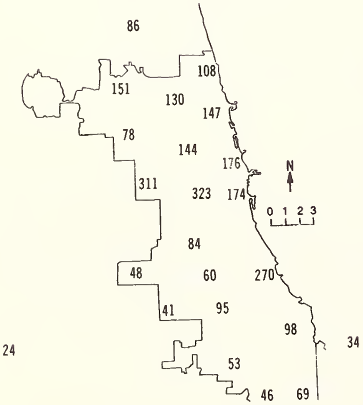

Figure 4. Distribution of bromine 10^{-9} g/m³.

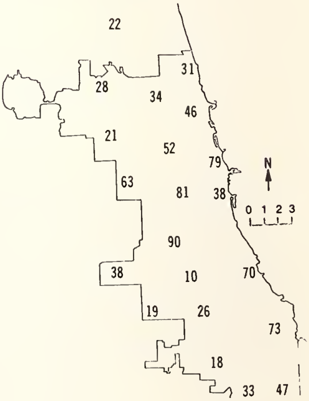

Figure 5. Distribution of manganese 10^{-8} g/m³.

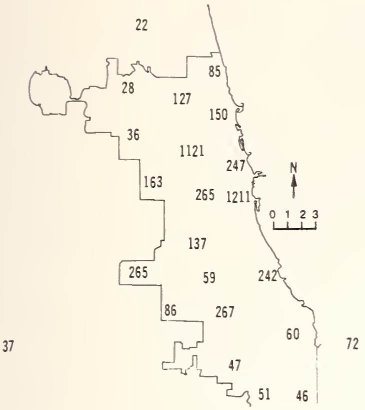

Figure 6. Distribution of vanadium 10^{-10} g/m³.

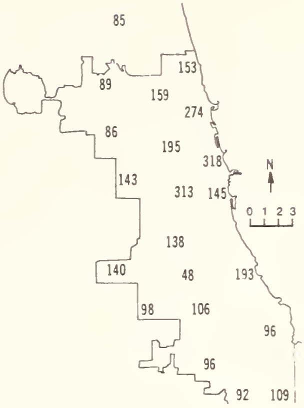

Figure 7. Distribution of aluminum 10^{-8} g/m³.

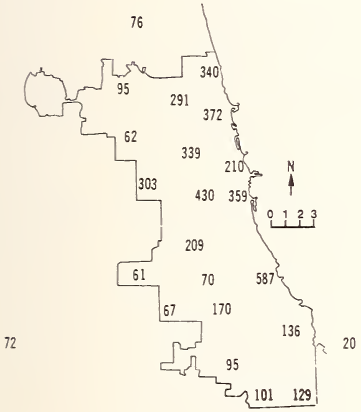

Figure 8. Distribution of chlorine 10^{-8} g/m³.

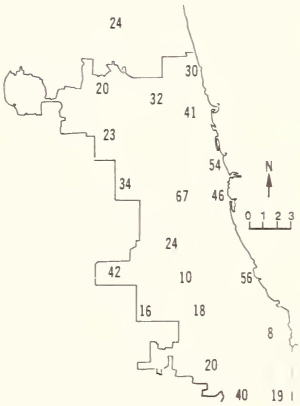

Figure 9. Distribution of sodium 10^{-8} g/m³.

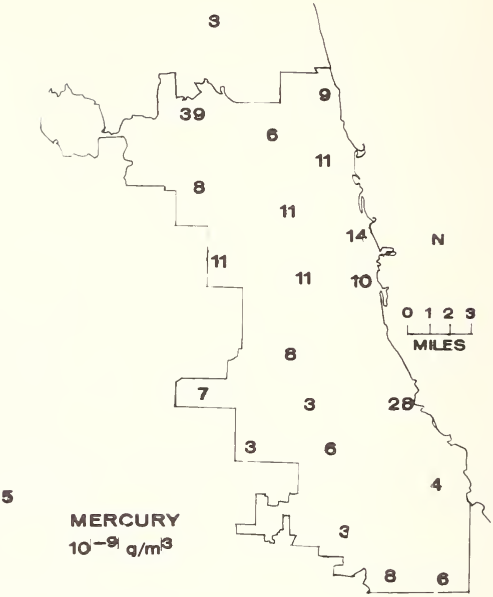

Figure 10. Scattergram of mercury observed in the air.

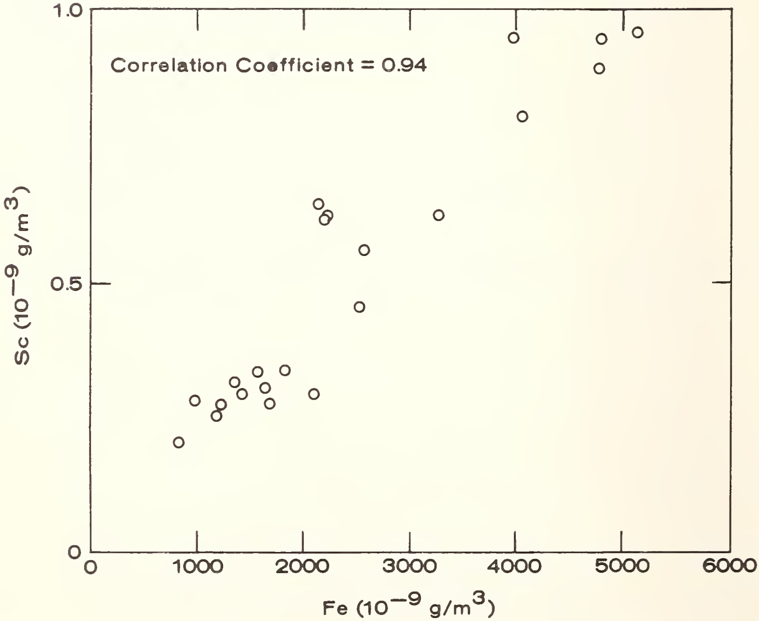

Figure 11. Iron *vs* scandium correlation in the air.

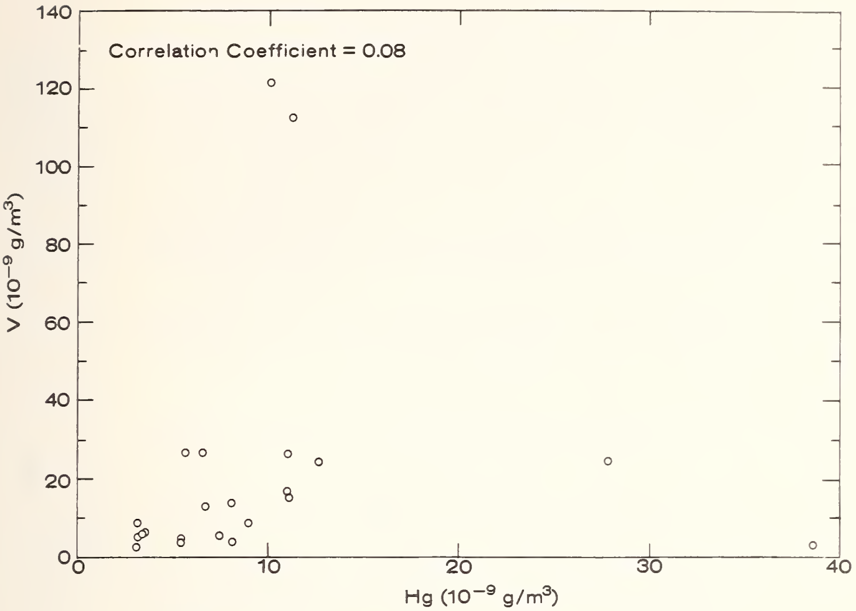

Figure 12. Mercury *vs* vanadium correlation in air.

Table 4. Nanograms per standard cubic meter of surface air in the Chicago Metropolitan Area.

Collecting stations															
Code	Name	Dust	Br	Mn	V	Al	Cl	Na	Hg	Cr	Zn	Fe	Sb	Sc	Co
Mg	Morton Grove	52600	86	220	2.2	850	760	240	3.2	11	190	1190	3.1	0.26	0.32
ANL	Argonne	27800	24	340	3.7	720	720	200	5.4	9.1	220	1240	1.7	0.27	0.49
A	Taft	49300	150	280	2.8	890	950	200	39.	13	360	1360	2.8	0.31	0.62
B	Lakeview	89900	150	460	15	2740	3730	410	11.	25	630	4070	12	0.81	1.99
C	Steinmetz	50300	78	210	3.6	870	620	230	8.1	8.7	300	970	2.8	0.28	0.81
D	Cooley[a]	128000	180	790	25	3180	2100	540	14.	37	760	5130	23	0.96	4.64
F	G.S.A. Bldg.	98600	170	380	121	1450	3590	460	10.	25	1070	3260	19	0.63	4.84
G	Crane[a]	101900	320	820	27	3130	4300	670	11.	28	1700	4800	55	0.95	3.16
H	Austin	70000	310	630	16	1430	3030	340	11.	16	510	2200	20	0.62	2.36
J	Kelly	74700	84	900	14	1380	2090	240	8.2	20	1210	2530	15	0.46	2.31
K	Lindbloom	32100	60	100	5.9	480	710	100	3.4	5.7	230	820	2.7	0.21	3.17
L	Hyde Park	144000	270	700	24	1930	5880	560	28.	25	960	4800	45	0.90	4.45
M	Stevenson	45700	41	180	8.6	980	670	160	3.2	9.4	610	1460	3.2	0.29	0.50
N	Calumet	53500	95	260	27	1060	1700	180	5.7	13	310	1550	3.9	0.33	0.82
O	Chicago Voc. S.	59300	98	730	6.0	960	1360	80	3.6	14	310	2090	5.9	0.30	0.69
P	Fenger	53500	53	180	4.7	960	950	200	3.2	15	220	1640	2.2	0.31	0.90
Q	Carver	69300	46	330	5.1	920	1810	400	7.5	20	230	1690	1.4	0.28	0.50
R	Clay	55700	69	470	4.6	1090	1290	190	5.5	13	920	1820	2.7	0.34	0.98
T	Sullivan	72400	110	310	8.5	1530	3400	300	9.0	16	410	2570	11	0.56	1.39
V	Logan Square	98400	140	520	112	1950	3390		11.	28	840	3980	24	0.95	4.40
W	Hale Franciscan	54500	48	380	27	1400	610	420	6.6	15	460	2120	7.6	0.65	0.86
X	Van Stuben	70600	130	340	13	1590	2910	320	6.1	15	430	2240	13	0.62	1.40
	TLV[b]	15×10^6		5×10^6	$.5\times10^6$	15×10^6			$.1\times10^6$	$.1\times10^6$	5×10^6	10×10^6	$.5\times10^6$		$.5\times10^6$

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[a] 48 hour run

[b] Workman's dose

Table 5. Correlation coefficients.

total dust	.69	.67	.46	.80	.84	.81	.42	.90	.64	.94	.81	.87	.78
	Br	.59	.28	.65	.77	.68	.50	.57	.60	.69	.85	.71	.61
		Mn	.16	.65	.54	.51	.23	.68	.70	.72	.68	.62	.49
			V	.29	.43	.34	.08	.51	.43	.45	.37	.51	.68
				Al	.67	.81	.24	.88	.66	.93	.76	.91	.61
					Cl	.72	.38	.68	.62	.81	.83	.79	.68
						Na	.33	.80	.63	.82	.81	.83	.60
							Hg	.31	.21	.34	.36	.33	.28
								Cr	.64	.94	.70	.86	.73
									Zn	.72	.80	.65	.62
										Fe	.84	.94	.77
											Sb	.83	.71
												Sc	.75
													Co

For 22 data points

Correlation coefficient	.36	.42	.49	.53	.65
Level of significance	.1	.05	.02	.01	.001

Table 6. Percent of element on the first paper when two cellulose papers are run back to back on the pump.

Station	dust	Br	Mn	V	Al	Cl	Na
Calumet	81	85	98	96	97	86	88
Crane	90[a]	87	98	97	99	79	93
Logan Square	80	87	100	97	100	70	
Hale	81						
Stevenson	78						

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[a] 48 hour collection period.

V. References

[1] Nelson, D. M., *et al,* Computer Program for Gamma-ray Spectrum Analysis. Biological and Medical Research Division, ANL 7136, 1965.

[2] Tabor, E. C., and Warren, W. Z., Distribution of Certain Metals in the Atmosphere of Some American Cities. A. M. A. Archives, Industrial Health **17,** 145-151 (1958).

[3] Duce, Robert A., *et al,* Iodine, Bromine, and Chlorine in the Hawaiian Marine, Journal of Geophysical Research **70,** 1775-1799 (1965).

[4] Lininger, Ronald L., *et al,* Chlorine, Bromine, Iodine, and Lead in Aerosols from Cambridge, Massachusetts, Journal of Geophysical Research **71,** 2457–2463 (1966).

APPLICATION OF ACTIVATION ANALYSIS AND Ge(Li) DETECTION TECHNIQUES FOR THE DETERMINATION OF STABLE ELEMENTS IN MARINE AEROSOLS[1]

N. D. Dudey and L. E. Ross

Argonne National Laboratory
9700 South Cass Avenue
Argonne, Illinois 60439

V. E. Noshkin

Woods Hole Oceanographic Institution
Woods Hole, Massachusetts 02543

I. Introduction

The concentration of many stable elements in over-ocean aerosols is presently unknown. A knowledge of these concentrations, and the variation of the elemental distributions as a function of location and time is important in understanding the sources of over-ocean aerosols and their transport mechanisms for both geochemical purposes and for defining general problems of air pollution and pollution control.

Recent advances in high resolution gamma-ray spectroscopy, notably the development of lithium-drifted germanium [Ge(Li)] detectors, has greatly extended the scope of neutron activation analysis (NAA). The purpose of this study was to evaluate the feasibility of elemental analysis of air borne particulate matter by means of NAA and Ge(Li) techniques. The concentrations of twenty trace elements in marine aerosols are reported, and suggestions for improvement of the technique are given.

II. Experimental

The aerosol samples were collected on microsorban polystyrene (Delbag) filter pads using a pump and filter assembly aboard Woods Hole Oceanographic Institution ships (WHOI) [1]. The sampling locations, dates, and volumes of air per sample are given in Table 1. Approximately

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[1] Work performed in part under the auspices of the U.S. Atomic Energy Commission.

Table 1. Sample collection data.

Sample number	Collection mid-date	Air sampling volume (cm^3)	Sampling location
3	2/23/66	1338	11°05 N43°42 W – 5°15 N23°28 W
4	2/14/66	546.1	14°55 N54°46 W – 10°48 N43°42 W
5	2/11/66	464.4	16°44 N61°25 W – 15°00 N54°46 W
6	4/28/66	449.8	10°21 N41°53 W – 13°31 N54°40 W
7	5/5/66	505.8	18°09 N64°45 W – 30°22 N67°18 W

10% of the surface of the original filter containing the filtrate was removed, weighed, and irradiated for 24 hours in the Argonne National Laboratory (ANL) CP-5 reactor. Blank filters were irradiated along with the samples.

The irradiated samples were counted on two detector systems, (1) a 20 cm^3 detector (having a resolution 3.2 keV FWHM for a 1.332 MeV gamma ray) with a 4096 channel analyzer system at ANL, and (2) a 30 cm^3 detector (4.1 keV resolution (coupled to a 1024 channel analyzer system at WHOI. The two systems were independently calibrated using at least nine standard gamma-ray lines whose energies are known to better than ±1 keV. Relative efficiencies were determined from ^{152}Eu, ^{154}Eu, and ^{160}Tb; absolute efficiencies were determined from absolutely calibrated ^{57}Co, ^{137}Cs, ^{54}Mn, and ^{60}Co standards.

Two samples were counted nondestructively. As was expected, the large quantities of ^{24}Na produced from the sodium in the over-ocean samples made quantitative determinations impossible.

A simple separation scheme was developed to remove the sodium. The samples were ashed, fumed with perchloric acid to incipient dryness and taken up in 6 *M* HCl. The solution was passed through a Dowex 1 × 10, 100-200 mesh anion exchange column, the column washed, and the resin transferred to a vial for counting. The effluent was neutralized to a pH of 5 and slurred with Chelex 100 resin while adjusting to a pH of 9. The Chelex resin was washed and transferred to a similar vial for counting. The sodium activity was reduced by a factor of 10^5. Equally important, the radioactive nuclides were almost equally divided between the two fractions; elements forming strong chloride complexes were retained on the anion resin while the remaining multivalent cations were adsorbed on the Chelex resin.

The samples were counted over a period of about six months. One of the Dowex and one of the Chelex fractions as well as a blank were selected to carefully follow the half lives of all nuclides present. Counting times ranged from 20-800 minutes.

The energies of each of the observed photopeaks were determined. The intensity of each peak was determined by adding 5 or 6 channels around the maximum of the peak. The "background" under each peak consists of the true background plus Compton scattered radiation from high energy gamma rays. This was subtracted from the total peak area by evaluating the level of the Compton radiation on the high energy side of the peak and assuming a flat response of the count rate per channel with respect to energy for Compton scattered events.

The accuracy of the Compton subtraction method was examined by counting a ^{57}Co standard with and without various levels of Compton background. Corrections for "background" contributions under a peak were found to be far more accurate when determined from the high energy side of the peak than when determined from both sides of the peak as is common in the analysis of NaI(Tl) spectra. If the "background" contribution was less than the counting rate in the net peak area, the accuracy in the peak activity was found to be better than 1%. For "backgrounds" about four times the net peak activity the errors were about 4%; and "backgrounds" in excess of 10 times the peak activity could result in errors exceeding 100%.

Each nuclide was identified on the basis of (1) the energy of the gamma ray (2) the half life, (3) the presence of associated gamma rays with the proper relative intensities, and (4) the presence of the nuclides on the appropriate ion exchange resin. Table 2 summarizes all nuclides identified in these measurements, and lists the pertinent cross sections and decay characteristics of each nuclide.

Corrections for trace elements in the polystyrene filter were made by irradiating and analyzing blank filters in a manner identical to the samples. Blank corrections were made by normalizing the blanks to the samples on a weight basis and subtracting the net counts in the blank from the net counts in the sample. A summary of the trace elements in the blank filters is given in Table 3 and compared to an analysis of similar filters reported by Shedlovsky and Paisley [2]. Photopeaks or Compton contributions were found in the blanks under photopeaks of many nuclides of interest in the samples. The half life and other decay characteristics did not, however, correspond to the isotopes of interest. Corrections were made to the sample counts for these activities and represent a limit to the sensitivity of the experiment, but because the identification is ambiguous they are not listed in Table 3.

III. Results and Discussion

A. RESULTS

The results of our analysis of five samples taken over the Atlantic Ocean in 1966 are reported in Table 4. In this experiment the relative

Table 2. Production and decay properties of nuclides detected.[a]

Element	Target isotope	Abundance (%)	Product nuclide	$\sigma(n_{th},\gamma)$ (barns)	Predominant gamma rays
Cerium	^{140}Ce	88.48	^{141}Ce	0.6	0.145
Lanthanum	^{139}La	99.91	^{140}La	8.9	0.487, 0.815, 0.923, 1.596
Samarium	^{152}Sm	26.63	^{153}Sm	210	0.103
Europium	^{151}Eu	47.8	^{152}Eu	5900	0.344, 1.408
Terbium	^{159}Tb	100.00	^{160}Tb	46	1.272
Ytterbium	^{168}Yb	0.14	^{169}Yb	11000	0.177
Hafnium	^{180}Hf	35.2	^{181}Hf	10	0.482
Scandium	^{45}Sc	100.00	^{46}Sc	23	0.889, 1.120
Chromium	^{50}Cr	4.31	^{51}Cr	17	0.320
Iron	^{58}Fe	0.31	^{59}Fe	1.1	1.098, 1.292
Cobalt	^{59}Co	100.00	^{60}Co	37	1.173, 1.332
Copper	^{63}Cu	69.1	^{64}Cu	4.5	0.511, 1.348
Zinc	^{64}Zn	48.89	^{65}Zn	0.46	1.115
	^{68}Zn	18.56	^{69m}Zn	0.1	0.440
Gallium	^{71}Ga	39.5	^{72}Ga	5.0	0.630, 0.835, 0.894, 1.465
Selenium	^{74}Se	0.87	^{75}Se	30	0.265
Indium	^{113}In	4.23	^{114}In	8	0.192
Antimony	^{121}Sb	57.25	^{122}Sb	6.06	0.564
	^{123}Sb	42.75	^{124}Sb	3.33	0.603, 1.690
Cadmium	^{114}Cd	28.86	^{115}Cd	1.1	0.490, 0.530
Gold	^{197}Au	100.00	^{198}Au	98.8	0.412
	^{186}W		^{187}W		0.479, 0.686
	^{146}Nd		^{147}Nb[b]		0.430, 0.533
	^{55}Mn		^{56}Mn[b]		0.845
	^{191}Ir		^{192}Ir[b]		0.317, 0.468

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[a] Data taken from reference [4].

[b] Nuclides identified but quantitative determinations were not possible.

Table 3. Analysis of filter blanks.

Element	Total (μg)	These filters (ppm)	Polystyrene[a] (ppm)	Delbag[a] (ppm)
Iron	5	12	5.0	3.9
Cobalt	4.1×10^{-3}	1.0×10^{-2}	28	7.4
Chromium	0.1	0.3	1.1	0.19
Copper	0.23	0.57	1.2	7.1
Gold	$<4 \times 10^{-6}$	$<1 \times 10^{-5}$	6.1	5.8
Zinc	1.6	4.0		
Cadmium	0.27	0.67		
Antimony	3.1×10^{-3}	7.7×10^{-3}		

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[a] See reference [2].

amounts of each element are thought to be accurate to better than ±15%. Errors in the weights of each element may be considerably larger due principally to errors in the neutron flux. Table 4 has been tabulated to show the micrograms of each element per cubic meter of air for sample 3 as well as the ratio of each element in each sample relative to the amount of that element in sample 3 for the 20 trace elements which were quantitatively identified.

B. Discussion

The trace elements found in this analysis of marine aerosols includes elements of considerable geochemical and public health interest. In Table 5 we compare some rare earth ratios found in marine aerosols to ratios reported for soil, shale and chondritic meteorites [5,6]. This comparison would indicate a soil type origin for rare earths in over-ocean aerosols. From Table 4 it is indicated that although the rare earth profiles appear similar, they are not identical, indicating contributions from various origins. Balashov and Khitrov [3] find that the rare earth content in aerosols collected over the northern part of the Indian Ocean is $1\text{-}2 \times 10^{-3}$ μg/m^3. When this was calculated to the mineral residue of the air suspension, it was found that the amount was equal to the concentrations of the rare earth in water suspensions implying aeolian transport may be a very important mechanism for the input of many trace elements to the ocean.

Table 4. Trace element concentrations.

Isotope	Sample 3 ($\mu g/m^3$)	Ratio of samples to number 3 4/3	5/3	6/3	7/3
Cerium	3.0×10^{-4}	--	0.26	6.8	0.074
Lanthanum	1.5×10^{-4}	0.42	0.22	7.3	0.25
Samarium	3.4×10^{-5}	0.37	0.13	5.9	0.05
Europium	4.4×10^{-6}	0.6	0.1	7.1	0.2
Terbium	8.9×10^{-6}	--	--	5.4	--
Ytterbium	5.0×10^{-6}	--	--	5.2	--
Hafnium	9.0×10^{-6}	--	--	5.5	--
Scandium	4.1×10^{-5}	0.55	0.12	7.1	0.26
Chromium	4.2×10^{-4}	--	0.6	1.8	0.3
Iron	0.23	4.8	0.32	4.2	0.53
Cobalt	8.7×10^{-5}	1.9	0.92	5.3	0.49
Copper	0.14	2.0	4.2	3.0	1.2
Zinc	2.5×10^{-3}	9.4	3.5	0.41	2.7
Gallium	1.4×10^{-4}	3.7	0.88	3.1	0.86
Selenium	3.6×10^{-5}	4.1	2.0	1.8	0.5
Indium	1.5×10^{-4}	0.9	4.2	1.4	5.6
Antimony	8.0×10^{-5}	4.4	8.2	1.5	15.0
Cadmium	3.0×10^{-4}	29	27	2.0	11
Gold	7.3×10^{-7}	7.7	2.0	7.7	4.0
Mercury	1.4×10^{-5}	7.2	3.3	4.7	6.1

Table 5. Rare earth ratios.

Elements	Sample 3	Sample 6	Russian[a] soil	Shale[a]	Chondritic meteorites[a]
Ce/La	2.0	1.9	1.9	1.9	2.8
Sm/La	0.2	0.2	0.35	0.18	0.70
Eu/La	0.03	0.03	0.02	0.051	0.25
Tb/La	0.06	0.04	0.02	0.031	0.16
Yb/La	0.03	0.02	0.02	0.087	0.57

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[a] See for example, references [5] and [6].

Our over-ocean samples contain such toxic elements as zinc, cadmium, mercury and selenium in amounts which are respectable percentages of their concentrations in the presumably contaminated air of several coastal cities.

The sensitivity of this type of experiment is primarily determined by the filter blank concentrations and secondarily by the relative intensities of the gamma rays in each spectrum. The accuracy could be significantly improved by measurements relative to a standard solution of composition similar to the samples. A short irradiation rapidly followed by counting would enable identification of shorter-lived nuclides having associated gamma rays. Application of these techniques are currently in progress.

IV. References

[1] Bowen, V. T., and Noshkin, V. E., NYO-2174-56 (1966).

[2] Shedlovsky, J. P., and Paisley, S., Tellus **18,** 499 (1966).

[3] Balashov, Yu. A., and Khitrov, L. M., Geochem. USSR, Eng. Trans. No. 9, 877 (1961).

[4] Lederer, C. M., Hollander, J. M., and Pedman, I., in Table of Isotopes, Sixth Edition, Wiley, New York (1967).

[5] Haskins, L. H., and Frey, F. A., Science **152,** 299 (1966).

[6] Haskins, L. H., Frey, F. A., Schmitt, R. H., and Smith, R. H., In Symposium Int. Assoc. Geochemistry and Cosmochemistry (Paris), p. 167.

ACTIVATION ANALYSIS APPLIED TO SEDIMENTS FROM VARIOUS RIVER DELTAS

A. J. de Groot and K. H. Zschuppe

Institute for Soil Fertility
Haren-Groningen, Netherlands

M. de Bruin and J. P. W. Houtman

Reactor Institute
Delft, Netherlands

P. Amin Singgih

Atomic Reactor Centre
Bandung, Indonesia

I. Introduction

In deltaic systems a transport of sand and fine-grained material occurs from the rivers *via* the fresh-water tidal area to the nearby coast. Especially sediments with diameters less than 50 μm can move with the water over large distances.

Much information has already been obtained about the transport of mud and its chemical behavior for a number of deltas in western Europe and in some tropical regions using manganese as an accompanying element [1-3].

Afterwards the change in concentration of the trace elements Fe, Cu and Co during the movement of the sediments from the rivers to the adjacent coastal areas was also investigated [4]. The trace elements were determined in acid extracts by conventional chemical methods. Such methods are cumbersome and do not necessarily lead to true values. It was therefore interesting to carry out some checks by nondestructive activation analysis. Moreover, this technique has provided extra information about the trace elements Cr, As, La, Sc and Sm. The results of this work are presented.

II. Experimental

Due to a preferred occurrence of the trace elements in the finest grain-size fractions, linear relationships are always found between the contents of trace elements and the fraction of particles <16 μm (expressed as a percentage of the $CaCO_3$—free mineral constituents) in samples from the same location. In Figure 1 these relationships are shown for a number of elements in sediments of the river Ems. These linear relationships make it possible to characterize the content of a specific trace element of a whole group of cogenetic sediments by a single value. This value represents the content obtained by extrapolation to 100% of the fraction <16 μm.

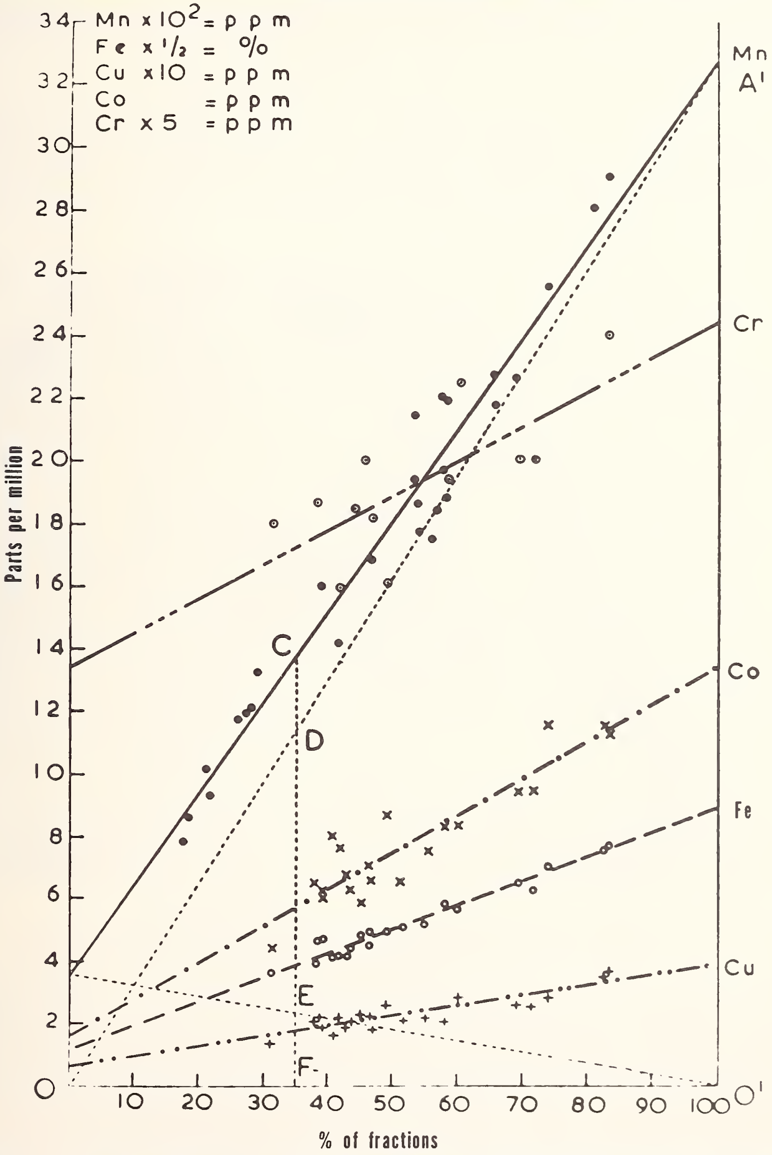

Figure 1. Linear relationships between trace element contents and percentage of fraction <16 μm (Ems sediments).

The activation analysis has been carried out at the Reactor Institute at Delft. Samples of the order of 400 mg were irradiated during short (1 hour for Mn, Sm, La, Zn, As) and somewhat longer (4 hours for Sc, Cr, Co) periods in the H.O.R. (neutron flux $3 \times 10^{12} \mathrm{n \cdot cm^{-2} \cdot sec^{-1}}$). After cooling (4 hours for Mn; 2 days for Sm, La, Zn, As; 2 weeks for Sc, Cr, Co) the gamma spectra were measured using a 16 $\mathrm{cm^3}$ Ortec Ge(Li) detector connected with an Intertechnique 4000 channel pulse-height analyzer.

III. Results

For a number of deltas, samples were taken from various regions ranging from the inner part of the delta with freshwater conditions to the outer marine environment (compare Figures 2, 4, 6). Results of the analyses are presented in Tables 1, 2, 3 and Figures 3, 5, 7. When comparing the data obtained from both chemical and activation analyses, a good agreement is found for manganese and also for the single value of zinc. However, for cobalt the data from chemical analyses are 25 to 50% too low, probably as a result of insufficient dissolution in the acid extraction procedure. Still, the conclusions regarding the behavior of this element during the transport of the sediments are not affected.

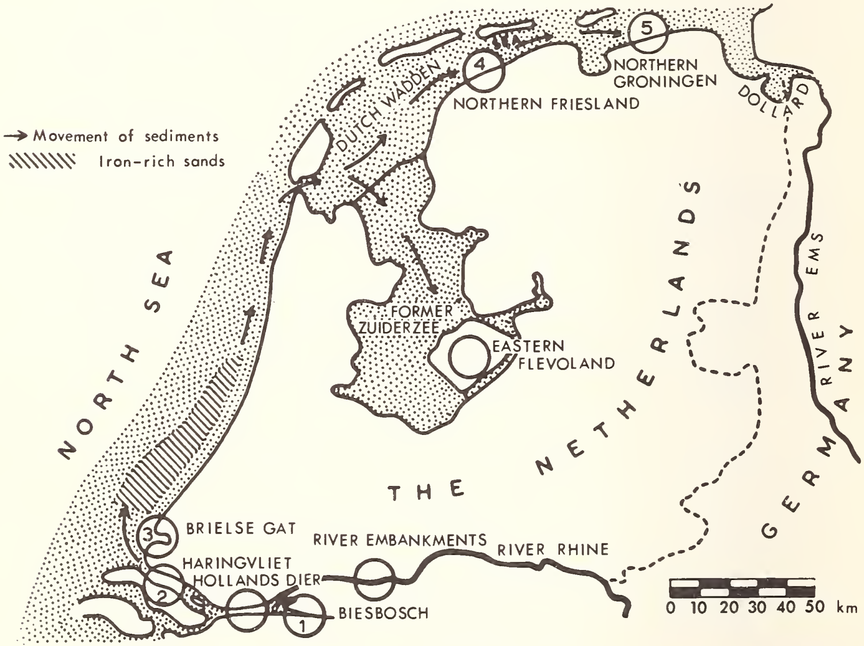

Figure 2. Rhine delta (Netherlands), movement of sediments.

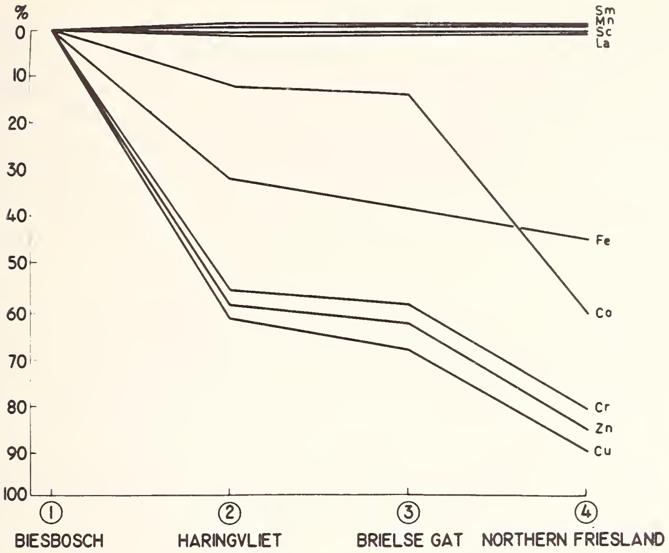

Figure 3. Mobilization of trace elements in the Rhine delta, expressed as a percentage of the original content.

A. RHINE DELTA (NETHERLANDS)

Sediments of the river Rhine are distinguished by the high Zn, Cr, Cu and As contents.

As shown in Figure 3, there are differences in the rate of mobilization of the various trace elements. From the river down to and including the sea as far as Friesland, the Mn, La, Sc and Sm contents remain constant. The Groningen sediments show a lower manganese content as a result of preceding deposition along the Friesian coast during which reduction occurs.

Table 1. Contents of trace elements, expressed in ppm, in sediments (extrapolated to 100% of the fraction <16 μm).

Rhine delta (Netherlands)

Rhine to sea ↓

		Fe × 10^3	Mn		Zn		Cr	Cu	As	La	Co		Sc	Sm
Location		CA[a]	CA	AA[b]	CA	AA	AA	CA	AA	AA	CA	AA	AA	AA
Biesbosch	(1)	54	2600	2600	3400	3900	760	470	310	80	24	43	12	7
Haringvliet	(2)	37	2600	2700	1500	ND[c]	300	180	ND	80	18	35	12	7
Brielse Gat	(3)	33	2600	3000	1300	ND	310	150	ND	70	18	33	11	8
Northern Friesland	(4)	32	2600	2500	400	ND	140	50	ND	80	10	16	12	7
Northern Groningen	(5)	35	1800	ND	300	ND	140	40	ND	(80)	8	16	13	(8)

[a] CA = chemical analysis.
[b] AA = activation analysis.
[c] ND = not detected.

The other elements undergo losses to varying extent during passage of the sediments to the lower courses of the delta. The most striking element in this respect is Fe, which reaches nearly its lowest state already in the Haringvliet. The Zn, Cr and Cu contents also undergo intensive decreases, which, however, need a longer distance to reach lowest values. Finally, Co does not undergo a more intensive mobilization before the marine area along the Wadden coast.

B. Ems Delta (Germany)

Sediments of the river Ems show substantially higher Fe and Mn contents when compared to those of the Rhine. To the contrary, the striking abundances of Zn, Cr, Cu and As found in the Rhine sediments are not observed here.

The sequence of mobilization of the trace elements is the same as found for the river Rhine, although the mobilization processes generally take place within a shorter geographical distance.

C. Chao Phya Delta (Thailand)

Here, one sample was prepared from various locations in the fresh water tidal area and one other from only one location in a fully marine area (Channel).

There is a remarkably low content of a number of elements in this tropical delta. Only the La and Sm contents are comparable with those of the western European deltas. On the other hand, Sc contents are much higher.

As appears from Figure 7 there is a much smaller mobility of trace elements in this tropical delta as compared to the mobility in deltas under temperate climatic conditions.

Table 2. Contents of trace elements, expressed in ppm, in sediments (extrapolated to 100% of the fraction <16 μm).

Ems delta (Germany)

			Fe × 10^3	Mn		Zn	Cr	Cu	La	Co		Sc	Sm
	Location		CA[a]	CA	AA[b]	CA	AA	CA	AA	CA	AA	AA	AA
↓ Ems to sea	Diele	(1)	112	3300	3300	700	180	150	80	22	40	12	9
	Leerort	(2)	53	3300	3300	400	160	50	80	17	24	14	9
	Ditzum	(3)	44	3300	ND[c]	300	120	40	80	13	21	14	10
	German Dollard	(4)	36	3100	ND	200	100	30	60	9	13	11	9
	Dutch Dollard	(5)	37	2100	ND	200	120	40	70	11	16	13	9

[a] CA = chemical analysis.
[b] AA = activation analysis.
[c] ND = not detected.

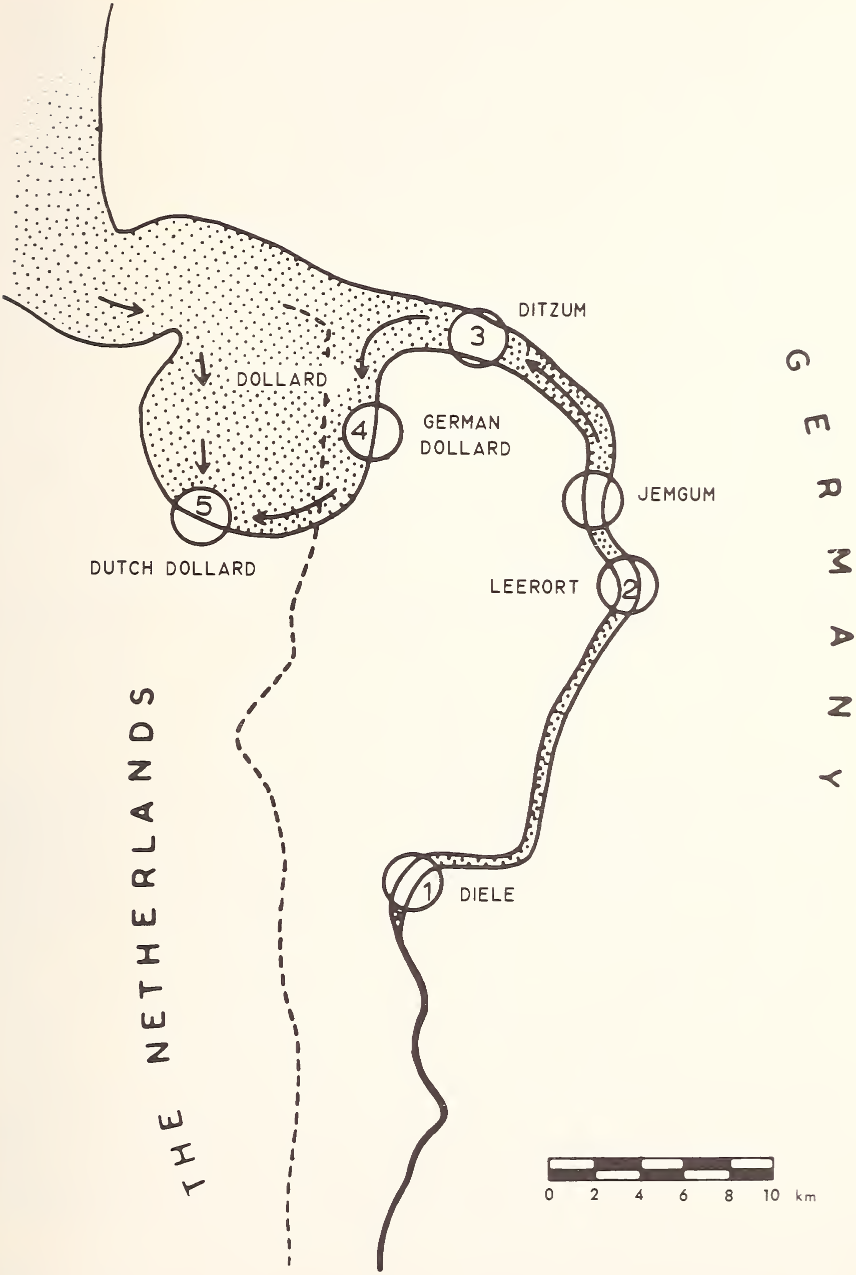

Figure 4. Ems delta (Germany), movement of sediments.

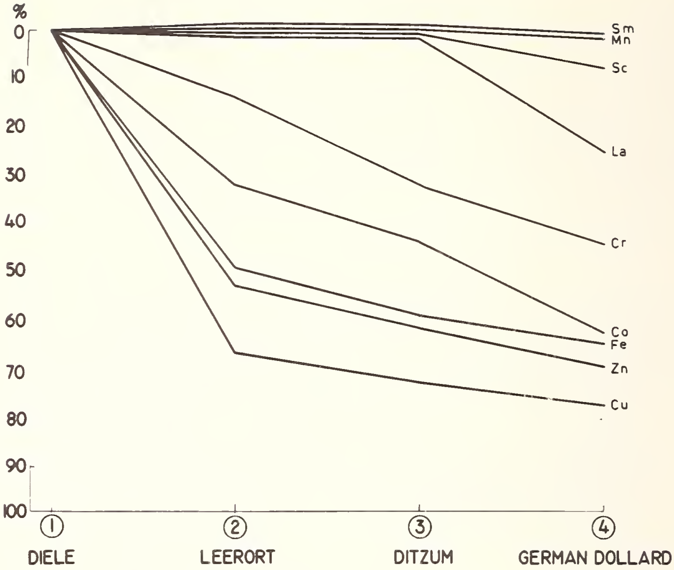

Figure 5. Mobilization of trace elements in the Ems delta, expressed as a percentage of the original content.

IV. Discussion

Extensive experimental work carried out in the Institute for Soil Fertility has produced evidence that the mobilization of trace elements takes place as organometallic complexes. From the fact that the degree of mobilization of the various trace elements largely corresponds with the series of Irving and Williams [5] it may be concluded that the stability of those complexes is the dominating factor in the intensity of the mobilization process. In the formation of the complexes the decomposition of organic matter present in the sediment particles plays an important role. The intensive decomposition of this matter in deltas under temperate climatic conditions can therefore be held responsible for the rapid mobilization of trace elements from sediments of Rhine and Ems. On the other hand, only a minor decrease in organic matter content was observed during transport of sediments to the lower courses of the Chao Phya delta. This is in agreement with the much smaller mobilization observed here.

Apart from this, the absolute concentrations of the various trace elements can be of strong interest for the agricultural aspects of Holocene soils, derived from mud sediments. The ultimate trace element contents of arable soils will depend on the original contents in the river solids and on the mobilization of the elements during the various stages of soil genesis.

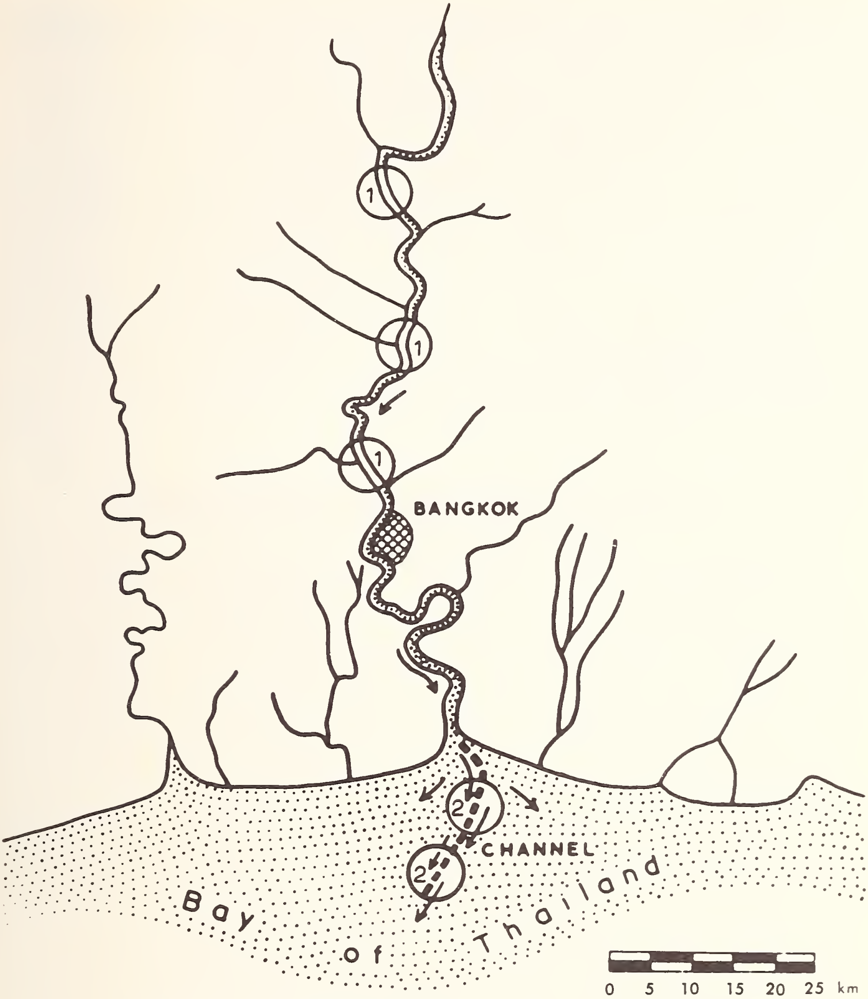

Figure 6. Chao Phya delta (Thailand), movement of sediments.

These processes may, under certain conditions, lead to concentrations of trace elements which are marginal for plant growth and animal health. For instance in the lower parts of the Rhine and Ems deltas, too-low copper concentrations are sometimes found.

Furthermore, manganese deficiency is found frequently to occur in the younger embankments of the Biesbosch area in spite of high manganese levels. This is caused by high zinc/manganese ratios and consequent suppression of manganese uptake.

As is shown, the level of trace elements is rather low in tropical areas while no mobilization takes place within the deltaic area. The

Table 3. Contents of trace elements, expressed in ppm, in sediments (extrapolated to 100% of the fraction <16 μm).

Chao Phya delta (Thailand)

↓ to sea

	Fe × 10^3	Mn	Cr	Cu	La	Co		Sc	Sm
Location	CA[a]	CA	AA[b]	CA	AA	CA	AA	AA	AA
River (1)	40	1800	100	50	90	12	21	19	8
Channel (2)	40	1300	100	40	80	13	21	19	8

[a] CA = chemical analysis.

[b] AA = activation analysis.

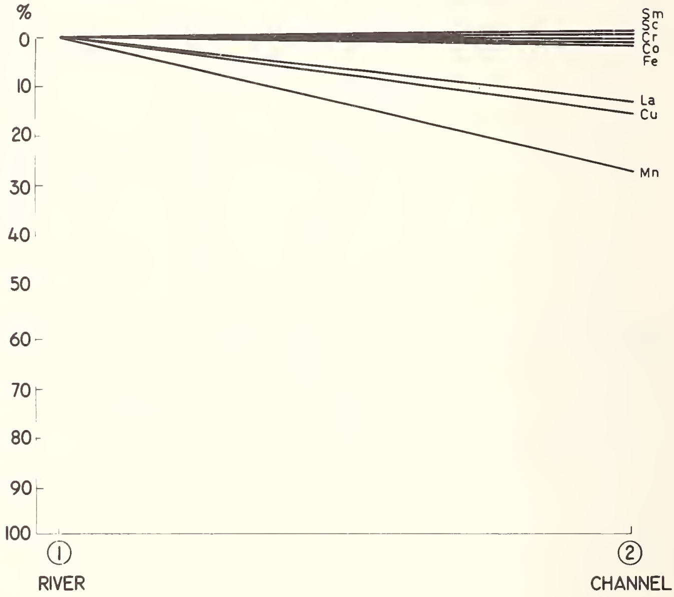

Figure 7. Mobilization of trace elements in the Chao Phya delta, expressed as a percentage of the original content.

consequences of this extreme behavior of trace elements for the cultivation of rice in these types of deltas (Amazon and Chao Phya) is now intensively studied. The pertinent information for such studies is very easily obtained by the nondestructive activation analysis of large numbers of samples on a routine basis. In this respect computer techniques are important and are being started at the Reactor Institute in Delft.

Moreover, activation analysis provides extra information about elements on which the study is not primarily focussed. As an example, the origin and consequence of high chromium and arsenic contents found in the Rhine sediment need further investigation. Also the differences observed in the content of manganese and scandium may be of geological interest. In this respect it is interesting to note that a preliminary qualitative inspection of our spectra has also revealed the presence of barium, indium, titanium, vanadium, europium, rubidium, cesium, hafnium, gold, ytterbium, thorium, cerium, aluminum, calcium, and lutetium in measurable quantities.

Finally, the information obtained can be used for selecting activated and immobile tracers for civil engineering and agricultural studies such as those concerning sludge deposition in harbors and soil transport during tillage.

V. References

[1] Groot, A. J. de, Versl. Landbouwk. Onderz. **7,** 1-164 (1963).

[2] Groot, A. J. de, Developments in Sedimentology (Amsterdam) **1,** 93-103 (1964).

[3] Groot, A. J. de, Proc. Dacca Symp. (UNESCO) Sci. Probl. Humid trop. Zone Deltas, pp. 65-71 (1966).

[4] Groot, A. J. de, Trans. Comm. II and IV, Int. Soc. Soil Sci., Aberdeen, 267-279 (1966).

[5] Irving, H., and Williams, R., Nature **162,** 746-747 (1948).

MEASUREMENTS OF MOVEMENTS OF SOLID SUBSTANCES IN WATER BY MEANS OF STABLE TRACERS AND ACTIVATION ANALYSIS

Carmelo Cappadona

Istituto di Applicazioni e Impianti Nucleari
Facolta di Ingegneria, University of Palermo
Palermo, Italy

I. Introduction

The study of the movements of solid substances in water is very important for the resolution of many problems; among these, those concerning navigation, the kinetics of erosion of the coasts, the covering with sand or slime of the shallow soundings and the migration of sand or gravel along the littorals. Radioactive tracers are very useful for these purposes, and their use has been widespread in the last years in many countries.

The principal applications carried out in Europe concern the study of the evolution of the beaches for sea storms (Cannes), the movements of sand in front of the harbors (Anverse, Bayonne, Figueira da Foz) and into the estuaries of some rivers and ship canals (Germany, Belgium) [1,2].

Work of great significance is generally involved in these applications and requires the use of considerable sums, special road transports, boats, helicopters and skilled labor. Moreover, the risk concerning the use of radioisotopes involves particular measures for protection; among these, the interdiction of fishing and sea bathing in the area of work. Lastly, the use of radioactive substances involves the task of obtaining special licenses and the observance of numerous regulations [1]. With the purpose of obviating the inconveniences mentioned above we have carried out an investigation using stable tracers that can be activated, thereby, doing away with many troubles.

In this paper a technique is described for the study of the movements of sand in Mondello Beach (Palermo, Sicily) which becomes more poor every year. The gulf area is about 9×10^5 m^2 and the littoral is a very famous summer resort.

II. Experimental

The choice of the stable tracer was made after a preliminary study indicated preference for Ag and Co. Neutron activation of some samples of the considered sand has not shown a significant presence of these elements. The use of silver is discussed further below.

A. TREATMENT OF THE SAND WITH THE STABLE TRACER OF AG

A sample of sand is cleared of foreign matter, treated with HCl dil. 1:3 and washed many times with demineralized H_2O until the chlorides are removed.

A solution of stannous chloride is added for the sensitization of the grains for the subsequent galvanic treatment, and a concentration of about 15% Ag is fixed into the sand. A better fixing has been obtained by treating the sand with a varnish (containing Ag as a colloidal dispersion) which is used in the ceramic industry for the metalization of porcelain which must be silverplated by the galvanic method. The treatment consists of mixing sand with varnish. The organic solvent is evaporated at room temperature and the sand is heated 3 hours at 400 °C.

A concentration of 47% Ag is thus obtained in the sand. Some of this metalized sand has been subjected subsequently to galvanic treatment for 10 minutes, but the concentration of Ag obtained was only 53%.

After the above treatment, the sand was submitted to abrasion tests for the determination of fixing efficiency. For this purpose samples of sand (50 g) were placed in bottles with 300 ml of sea water. The bottles were sealed and supported in a rack which rotated around a horizontal axis at 20 rpm. The water was removed every 12 hr and the total time of motion was 120 hr. At the end of the test, the samples were washed with H_2O dem. and assayed. The losses of Ag did not exceed 5%.

B. AMOUNT OF AG TO BE FIXED IN THE SAND

The sand of the considered coast is about 9×10^4 m^3, which is equivalent to 2.5×10^8 kg (density 2.7). By using 7.5 kg of Ag, a dilution equivalent to 30 μg/kg of sand is obtained.

From the results related above, the amount of sand necessary to fix Ag, is between 200 and 400 kg.

After the above treatment this sand will be scattered in the sea along the littoral and after some time, many samples of 1 kg amount will be drawn in some areas of the coast and will be analyzed for Ag.

C. EXTRACTION OF AG FROM THE SAND AND EVALUATION OF THE YIELD

1. A sample of 100 g of sand tagged with ^{111}Ag ($T_{1/2} = 7.6$ d; gamma 243-340 keV) has been prepared by sensitizing the grains with stannous

chloride and placing the grains into an electrolytic bath with a solution containing 100 μCi ^{111}Ag carrier-free (nitrate) and 50 mg $AgNO_3$ carrier. A specimen, C_1^*, of 0.1 g is drawn from this sand, washed and dried, and its activity A_1 is measured.

2. The activity, B, of a solution, S, containing 5 nCi ^{111}Ag is measured. 0.1 g of sand is added, and the sample is dried and its activity, B_1, measured. In this way it is possible to know the number of μCi corresponding with the activity, A_1, and the amount, P_1, of Ag carrier contained in the sample C_1^*.

3. The extraction of Ag from the samples taken along the coast is carried out by coprecipitation with a suitable carrier. Thallium has been chosen for its good yield of extraction and for its not interfering in the measurement because it gives rise to a pure beta emitting radioisotope.

The specimen, C_1^* is added to a sample, C, of 1 kg of washed sand. After mixing the sand is treated with portions of dilute HNO_3. It is not necessary to etch completely the grains for the extraction of Ag. To the filtrate, F, obtained are added 100 mg $TlNO_3$ and HCl in excess in order to precipitate Tl and Ag chlorides. To obtain a specimen for the irradiation, as free as possible from impurities, the precipitate is dissolved with H_2O containing NH_4OH and the liquid is treated with $(NH_4)_2S$. With this treatment the Tl and Ag sulphides are formed. The suspension is centrifuged and the residue is washed heated and treated while it is hot HNO_3. The Tl and Ag nitrates are obtained and the sulphur is separated. The filtrate, C_2^*, is made to the same volume of the solution, S, and is measured under the same conditions. The activity, A_2, of the same sample, C_2^*, due to ^{111}Ag extracted from the sample of sand, allows measurement of the yield, R, of extraction in amount, P_1, of Ag carrier, and, therefore, it is possible to know the amount, P_2, contained in C_2^*.

4. The specimen C_2^* is now ready for the neutron irradiation with a suitable standard, *i.e.* a solution containing the same amount P_2 of Ag (internal standard) present in C_2^* and some tens of mg $TlNO_3$.

The irradiation can be made at once if the measurements of activity are carried out with discrimination between the photoelectric peaks of ^{108}Ag from ^{111}Ag. However, it is possible to allow first the decay of ^{111}Ag for a proper time.

D. CALCULATIONS

The irradiated sample, C_2^*, gives rise to the activity, A_3, from ^{108}Ag that is the sum of the activities of the internal standard (P_2) and of eventual Ag extracted from the sample C. The irradiated standard gives rise to the activity, A_4, and is obtained by the equation:

$$\frac{A_4}{P_2}=\frac{A_3}{P_x}$$

where, P_x, is the weight of P_2 and Ag extracted from the sample C.

Correcting for the yield, R, we have: $P_xR = P_1 + X$; $X = P_xR - P_1$ where X is the unknown weight of the stable tracer Ag contained in the sample of sand.

III. Results and Discussion

The analysis of stable tracer contained in the collected samples, allows hydrologists to obtain significant information about the direction of the sand movements. The quantitative data that are obtained by this method present the possibility of carrying out a more complete study about the causes of the impoverishment of sand on the beach. Moreover, the cost of the research is greatly reduced, and measures for the protection and prohibition of people on the coast are no longer necessary.

IV. References

[1] Eurisotop-Euratom, "Use of Radioactive Tracers for the Determination of Movement of Solid Substances in Water".

[2] I.A.E.A., "Radioisotopes in Hydrology, Vienna, 1963.

SPECIFIC ACTIVATION ANALYSIS TECHNIQUES AND METHODS FOR THE ASSAY OF TRACE SUBSTANCES IN AQUATIC AND TERRESTRIAL ENVIRONMENTS

G. W. Leddicotte

Nuclear Engineering & Radiological Sciences
University of Missouri
Columbia, Missouri

I. Introduction

The analysis of our environment in the interest of reducing all pollutants that can affect man's well-being is a challenge to all scientists. Analytical chemists have an important role to play in these interests because it becomes their responsibility to provide analytical methodology for trace substance research so that they can assay an material from the environment for these substances even when they are in concentrations as small as 10^{-12} or 10^{-13} gram. Accurate and precise data on substances in these concentration ranges are essential and must be combined with findings from studies being carried out by toxicologists, epidemiologists and other scientists who are concerned with pollutants in the environment, so that a more knowledgeable interpretation can be made to define the tolerance levels of pollutants in urban and industrial environments.

Analytical methodology for the determination of trace substances in concentrations of parts per million (ppm) or less is somewhat limited. Activation analysis is generally considered to be useful method for trace inorganic species in such low concentrations. In the pollutant investigations considered in this paper, neutron activation analysis was the method of choice. Its sensitivity in a high flux nuclear reactor and its specificity for elemental species has made it possible to contribute significantly to specific areas of health related research and environmental science.

II. Experimental

In these studies, samples of water, soil, stream sediments, dusts, vegetation and similar materials from aquatic and terrestrial environments have been assayed for unusual, as well as common, elements. In particular, these studies have been concerned with the potential hazards and significance of these elements as environmental pollutants when they are used as pesticides or fungicides, catalytic or excitation agents, or as part of an industrial process.

In order to understand the aqueous chemistry of these species (as applicable to aquatic environments) and the physiological effects of the uptake of some of these species by man and animals, a comprehensive neutron activation analysis method has been developed for assaying these materials. The method involves both nondestructive and radiochemical processing of the irradiated materials. As required, chemical separations involving either volatilization, precipitation, solvent extraction, or ion exchange are used to complete the radiochemical portion of the assay method.

In all of the work to be reported, the radioactive products of thermal neutron bombardments have been used as the "fingerprints" of the stable species being determined. The half lives of these radioactive species vary from a few minutes to years. Gamma-ray spectrometry is used to complete the assay of the induced radionuclide species.

A. Apparatus

The pneumatic tube system of the University of Missouri research reactor was used in these activation analyses. At its 5 Megawatt power level of operation, a flux of at least $5 \times 10^{13} n \cdot cm^{-2} \cdot sec^{-1}$ is obtained in this facility. Variable irradiation periods ranging from 30 seconds to 20 minutes have been used in this work. All sample specimens are encapsulated in individual polyvials. Each polyvial after being sealed with a heated soldering iron, is placed into a polyethylene "rabbit" for the irradiation.

All radioactivity measurements are made by the use of a radiation detection and measurement system employing a multichannel gamma-ray spectrometer.

B. Reagents

As applicable, reagent grade chemicals are used in the radiochemical separations. Comparator samples of the element of interest are prepared from refined chemical compounds. In most instances the nitrate form of the element is used.

C. Procedure

After encapsulation and the choice of an irradiation period, the materials are irradiated. Initially each irradiated specimen is transferred to a plastic culture tube for a nondestructive gamma-ray spectrometer measurement. Either a 3 in. × 3 in. NaI(Tl) or a 10 cm^3 Ge(Li) radiation detector can be used for these measurements. The accumulated data are recorded as an X-Y plot and as either a numerical printout on an electric typewriter, or as a punched tape for computer processing.

Following these tests, the sample can be chemically processed or returned to the reactor for an additional irradiation period before chemical processing. The *general* procedure followed, involves (1) dissolution of the sample material (if required), (2) addition of carrier elements, (3) a volatilization step, and (4) further separations involving precipitation, solvent extraction and ion exchange, and (5) an aqueous fraction. Such a procedure provides at least six (6) major fractions. As applicable, each fraction can be broken down into smaller groups of elements or individual elements through the use of additional chemical separation steps involving solvent extraction, precipitation or ion exchange. Following each group or individual element separation, the radioactivity is measured by a gamma-ray spectrometer.

Comparator samples composed of diverse materials and multiple elements are irradiated and processed in a similar manner. The radioactivity data of the comparator and the test sample are compared to provide concentration data for the element(s) of interest.

III. Results and Discussion

The results presented in Tables 1-5 are *typical* of data obtained in the activation analysis of the various materials considered of importance to this environmental investigation. The data given in Table 1 for water analyses are of special importance to researchers in medicine who are attempting to relate anomalies of trace element distributions to the epidemiology of various diseases. Similarly, the data given in Table 2 are important to epidemiologists as well as to industrial users who require

Table 1. Trace elements in deep spring waters.

	Concentration, ppb		
Element	Sample 1	Sample 2	Sample 3
Copper	2.	11.	5.
Manganese	0.4	37.	9.
Chlorine	2400.	900.	800.
Aluminum	6.	620.	1500.
Iron	220.	240.	110.
Zinc	17.	16.	0.5
Selenium	2.	2.	1.
Thorium	0.2	0.3	0.1
Cobalt	0.2	0.2	0.1
Cesium	0.07	0.05	0.05

Table 2. Activation analysis of industrial waters.

A. Raw supply

Element	Concentration, ppm
Chlorine	0.5
Bromine	0.015
Copper	0.003
Manganese	0.0014
Barium	0.005
Strontium	0.4
Sodium	6.4

B. After deionization process

Element	Concentration, ppm
Bromine	0.01
Copper	0.0001
Manganese	0.0005
Sodium	0.01

Table 3. Chloride pesticide residues.

Sample	Cl^- concentration
A	10, 9.9 ppb
B	100, 101 ppb
C	200, 205 ppb
Atrazine	6.1 ppm
Sirazine	2.6 ppm

pure water for certain chemical processes. A continuous investigative program of water sources is being carried out.

Table 3 gives data on the determination of trace amounts of chloride pesticide residues in plant materials. A rapid nondestructive method involving only the measurement of the 1.62 and 2.12 MeV gamma radiations from 38 minute ^{38}Cl were used to collect these data. Other species observed in these samples included ^{64}Cu, ^{76}As, ^{56}Mn and ^{24}Na. A similar procedure was used to determine the bromine pesticide residue content of vegetation given in Table 4. In addition to trace bromine, assays of the Mg, Mn and Cu contents of these materials were made; these data are also shown in Table 4.

Table 5 reports some of the data observed in the assay of soils for unusual element concentrations. The importance of these species to pollutant problems are unknown at present but the data are being evaluated by ecologists and environmental scientists.

Table 4. Pesticide residue and trace bromine, manganese, magnesium and copper in vegetation.

		Element concentration, ppb			
Sample	Sample weight	Bromine	Magnesium	Manganese	Copper
ML	1.24 mg	1	2.6	200.	56.
Al	5.1 mg	5	0.3	115.	76.5
C	14. mg	10	0.4	113.	34.3
DH	9.3 mg	8	1.1	125.	26.3
DL	14.9 mg	10	1.7	184	78.4
AH	0.22 mg	1	7.6	224	165.1

Table 5. Cerium, lanthanum, scandium, and thorium in soils.

	Concentration, ppm			
Soil type	Cerium	Lanthanum	Scandium	Thorium
Litz	70, 85	49, 65	5, 12	26, 40
Montevallo	290, 300	62, 78	26, 30	54
Allen Loam	35	28	3	25, 34
Lehen	63	57	2, 5	16, 23
Prader	50	35, 50	4, 5	22, 27
Emory	80	85	5, 5	26, 37

In addition to such efforts as these, data have been obtained on (1) the presence and absence of specific elements from municipal water systems in a number of cities in the United States, (2) the effect of trace elements in water and forage (*e.g.* treated with bromine fungicide materials) and their influence on animal physiology, (3) the toxicity relationship of arsenic, selenium, mercury, cadmium and antimony to all environments, and (4) the control of contaminants in animal environments. Data from and general information about these projects will be given as part of the formal presentation of this research.

The specificity and sensitivity already afforded by the work carried out on this activation analysis methodology is significant in that it makes it possible to interpret the chemistry and biochemistry of such materials and to serve as a practical method to identify potential hazards to the environments of man and animals.

POST-SAMPLING ACTIVATION ANALYSIS OF STABLE NUCLIDES FOR ESTUARY WATER TRACING

J. K. Channell and P. Kruger

Civil Engineering Department
Stanford University
Stanford, California

I. Introduction

The feasibility of using stable, high neutron capture cross section, rare earth elements (REE) as external tracers in estuarine waters is being investigated. These tracers, when analyzed by post-sampling neutron activation analysis, have calculated sensitivities of 10^{-3} to 1 ng/sample compared to 10 to 100 ng/liter with fluorescent dyes. The method utilizes the inherent sensitivity of radioactivation analysis and avoids introducing radioactive materials into the estuary.

The development of the method includes considerations of: (1) the most suitable tracer element; (2) an optimum radiochemical-activation-counting procedure for estuarine waters; (3) the natural background concentrations of the element and its variability in the San Francisco Bay estuary system; (4) the persistence of the element in estuarine waters containing suspended solids and bottom muds; and (5) a comparison of tracer plus analytical costs between this method and fluorescent dyes.

An element chosen for an estuarine neutron activation tracer should have: (1) a low natural background in estuarine water, (2) favorable nuclear properties, (3) persistence in the estuarine environment, and (4) reasonable cost. Several of the REE have good nuclear properties and are reasonable in cost. Concentrations of 0.1 to 10 ng/liter have been reported from activation analyses of open-ocean water samples [1-3]. This method adapts the procedures reported for open-ocean analysis to separate the REE as a group from estuarine water samples. It was recognized that large suspended sediment and biological concentrations in estuarine water might interfere with the analysis.

II. Experimental

Pre-irradiation treatment is necessary to remove gram quantities of dissolved minerals from nanogram quantities of REE. Carrier free ^{88}Y is added to a 10-liter sample of estuarine water. The sample is filtered through a glass-fiber filter and then acidified to pH 1 to 2 with HCl. Then 150 mg of purified iron is added as a carrier for the REE. The pH is raised to >8 by slowly bubbling NH_3 gas into the solution. Elapsed time between acidification and attainment of pH >8 is less than 1 hour. The sample is heated at 45 °C for several hours. After aging and settling, the $Fe(OH)_3$ precipitate is centrifuged and the supernatant discarded. The dissolution of the precipitate is standardized by mixing with a few ml of 7 *N* HCl for 10 minutes and centrifuging for 7 minutes. The residue is discarded. The solution is poured onto a 0.7 cm × 15 cm anion (AG 1 × 8, 100-200 mesh, prewashed with 7 N HCl) exchange column and washed with about 10 ml of 7 N HCl. This step removes the iron and any coprecipitated uranium. The sample is further purified by adding 40 mg Fe, precipitating with NH_3 gas, centrifuging, discarding the supernatant, and dissolving the precipitate in 7 *N* HCl. The sample is evaporated to a 2 ml volume and transferred to a 7 ml polyethylene vial for activation.

Three sample vials are irradiated concurrently, with a europium neutron flux monitor attached to the top of the vials. Irradiations of 2 to 5 hours are made in the Stanford University 10 kW pool-type reactor, which has a thermal neutron flux of $1 \times 10^{11} n \cdot cm^{-2} \cdot sec^{-1}$ and a fast neutron flux of $2.3 \times 10^{11} n \cdot cm^{-2} \cdot sec^{-1}$.

Post-activation radiochemistry removes non-REE radioactivity. The sample is passed through 0.7 cm × 10 cm cation (Dowex 50 × 8, 50-100 mesh) exchange resin converted to the barium form. The column is washed with 0.08 *N* NaCl solution until the elutant contains no ^{24}Na activity (about 200 ml to 300 ml) and then washed with 0.05 *N* $MnCl_2$ until ^{56}Mn activity is removed (250-350 ml). The REE remain on the resin. After washing, the resin is transferred to a 7-ml polyethylene vial for gamma-ray scintillation counting with a 3 in. × 3 in. NaI well crystal and a 400 channel gamma-ray spectrometer.

The net activity under both the 0.75-1.10 MeV and the 1.45-1.71 MeV photopeaks is determined by the Compton Continuum Subtraction Method. A sample is counted several times over a 5-day period and the net activities plotted on a radioactivity decay curve. Lanthanum-140 activity is determined from the 1.45-1.71 MeV plot. Europium-152 activity is determined from the 0.75-1.10 MeV plot after resolving the decay component of ^{140}La and any contaminants that are present. Chemical yields of individual REE are obtained by measuring the ^{88}Y activity after decay of induced activity, and correcting for variations in flux and cation-column fractionation.

III. Results and Discussion

The method was developed from studies with artificial sea water and from preliminary investigations of REE background concentrations in

San Francisco Bay. Artificial sea water samples minimized potential problems from suspended biological and inorganic materials during the initial development stage.

The chemical yield of the ^{88}Y tracer averages 60-70% before activation. In several samples, stable europium was also added and its yield found to be quantitative with the ^{88}Y yield. It is thus assumed that the yields of REE naturally present in the water are also quantitative. Due to the high ionic strength of the sample solution, only 25-60% of the ^{88}Y tracer is retained on the post-activation cation exchange column. Radioisotopic tracers showed that the retentions of europium and lanthanum are 1.32 and 1.54 times the ^{88}Y retention. Thus overall apparent yields of europium and lanthanum range from 25 to 50%.

The post-activation cation exchange procedure results in essentially complete removal of the large amounts of ^{38}Cl. There is a significant, but at times incomplete, removal of ^{24}Na and ^{56}Mn. The REE not retained on the column are present in the first few milliliters of eluant.

At this activation sensitivity, the only two REE radionuclides identifiable in San Francisco estuary samples are ^{152}Eu (both the 9.3-hour and 12.7-year isomers) and 40.2-hour ^{140}La. The major contaminant is 35.3-hour ^{82}Br and at times there are minor amounts of 15-hour ^{24}Na and 2.58-hour ^{56}Mn. Except for ^{82}Br, the counting rates of these four nuclides, plus the ^{88}Y tracer can be determined in a single spectrum due to differences in half lives and the existence of secondary peaks. Bromine-82 is difficult to separate from ^{140}La, and its presence must be minimized in order to reduce the "apparent" lanthanum background. Concentrations of europium and lanthanum are computed by the comparator technique, and the activities of sample and comparator are corrected for differences in neutron flux and chemical yield.

Table 1 gives the results of San Francisco Bay samples and blanks run by a modification of this procedure (samples not filtered or reprecipitated). The data indicate that reproducibility of the order of ±25% can be obtained in similar estuarine waters, provided the samples are treated identically. The two estuary samples were taken two hours apart from the same location. Their electrical conductivity and turbidity agreed within 5%. The two blank samples (identical analyses with demineralized water) were prepared and activated at different times. The data show natural background concentrations of 10 to 25 times the concentration of reagent blanks.

Table 2 shows the effect of varying the time of acid contact and inclusion of filtration or reprecipitation steps influences the apparent concentrations. Since several variables are included in these samples their relative importance is not certain. It has been reported that REE can be leached from acidified ocean sediments [1]. Both the filtration and re-

Table 1. Results of similar samples analyzed identically.

	Concentration, 10^{-9} grams/liter	
Sample	Europium	Lanthanum
C.S. #1	17	280
C.S. #2	13	150
Blank #3	0.62	37
Blank #4	0.42	25

Table 2. Effect of variable analytical procedure on apparent concentration.

	Concentration (ng/liter)		Time of residue contact with acid			Comments
Sample[a]	Eu	La	Dilute A	Conc. A	ml Residue	
S.W. #1	1.7	28	3 d	4 h	0.3	Reprecipitated and dissolved in dilute HNO_3 before activation. Not filtered.
S.W. #2	3.3	35	4 d	10 d	0.1	Sample filtered 8 hours after acidification. Reprecipitated and activated in dilute HNO_3.
S.W. #3	4.9	~50[b]	19 d	17 min	0.3	Not filtered or reprecipitated. Activated in concentrated HCl.

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[a] All samples taken from the same 50 liter drum.

[b] The sample also contains ~570 ng/liter of ^{82}Br (expressed as apparent lanthanum) which makes the lanthanum concentration very approximate.

precipitation steps reduce the quantity of non-REE that are activated and have been shown to be very effective in reducing sodium and bromine contamination.

Figure 1 shows gamma spectra of one sample which has 2.7 μg/l of added lanthanum and two samples which are background only. The minimum detectable amount (MDA) of tracer with this background and variability is 300-400 ng/l.

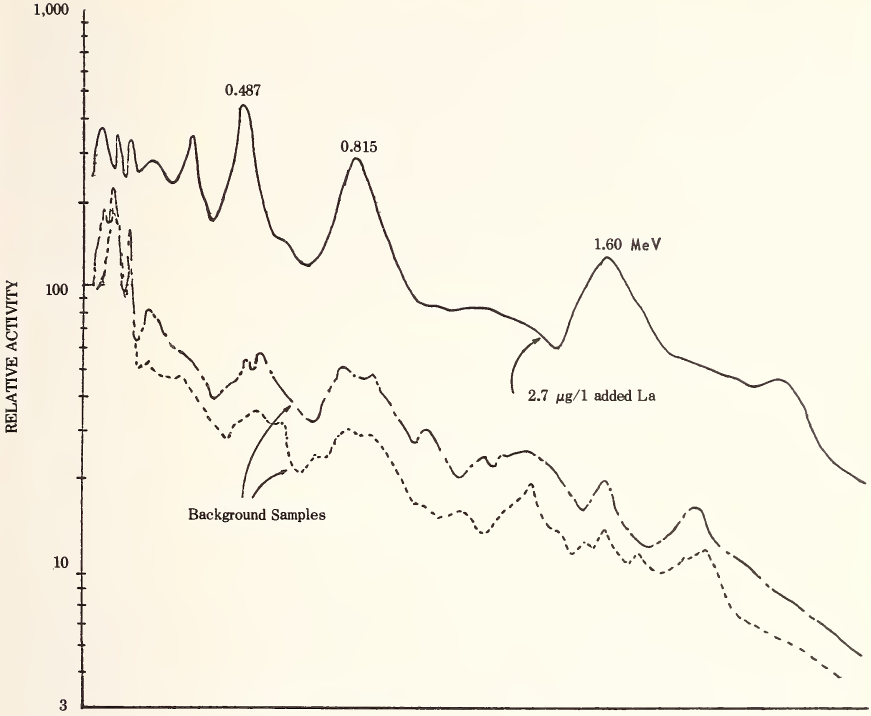

Figure 1. Gamma spectrum of rare earth group in estuarine water ($\Delta t_0 = 4.8d$).

Current studies are aimed at determining variability of the analysis and of the natural background concentrations for lanthanum and europium in the San Francisco Bay estuary. This variability, rather than the mean concentration, will determine the minimum detectable amount (MDA) of tracer. The MDA may be defined as 2 × total standard deviation, where:

$$MDA = 2\sigma_T = (\sigma_A^2 + \sigma_B^2)^{1/2} \qquad (1)$$

The analytical error (σ_A) is determined from reproducibility of duplicate samples while the background error (σ_B) is determined from samples taken at varying seasons, locations, and tidal conditions. It is possible that variability in the background concentration is not purely random, but is related to characteristics of the water. If so, σ_B could be significantly reduced by relating concentration to other water quality parameters, such as electrical conductivity, a measure of dissolved solids, or turbidity, a measure of suspended solids.

IV. References

[1] Goldberg, E. D., Koide, M., Schmitt, R. A., and Smith R. H., "Rare Earth Distributions in the Marine Environment", J. Geophys. Res. **68,** 4209-4217 (1963).

[2] Høgdahl, O. T., "Distribution of the Rare Earth Elements in Sea Water", NATO Research Grant No. 203, Semiannual Progress Reports No. 1-6, April 1965-March 1968.

[3] Hayes, D. W., Slowey, J. F., Hood, D. W., Section 4 of "The Chemistry and Analysis of Trace Metals in Sea Water", Texas A & M University, TID-23295, 1966.

NEUTRON ACTIVATION ANALYSIS OF VANADIUM IN NATURAL WATERS

K. D. Linstedt

Civil Engineering Department
University of Colorado
Boulder, Colorado

Paul Kruger

Civil Engineering Department
Stanford University
Stanford, California

I. Introduction

The significance of trace elements in supply waters has become of considerable interest in water quality control research because of the increased sensitivities with which these elements can be studied. The means for ascertaining both the adverse and beneficial physiological effects of these elements has accompanied the development of sensitive atomic absorption, spectrographic, radioactivation, and radiotracer methods of analysis.

Vanadium generally occurs as a trace element in supply waters. It is of interest in water quality control research because of its possible physiological significance. This element is of particular medical interest because it has been shown at low intake levels to act in the inhibition of cholesterol synthesis.

The occurrence and behavior of vanadium in several natural waters have been investigated as part of a study of its fate in domestic supply waters. Analyses for vanadium in water are commonly made by spectrographic methods. However, the dissolved solids concentrations in some natural water systems, such as the Colorado River, severely limit the sensitivity of spectrographic analyses. Neutron activation analysis provides a suitable analytical method under these conditions because of the inherent sensitivity and isotope selectivity available. Radiochemical separation methods and gamma-ray spectroscopic analysis are combined to achieve a maximum sensitivity in excess of that required to measure vanadium in natural water containing large amounts of dissolved solids.

II. Experimental

The high ratio of total dissolved solids to vanadium in natural waters necessitates, for quantitative activation analysis of general applicability, the inclusion of preirradiation sample concentration in addition to postirradiation radiochemical separations. The preirradiation concentration increases the vanadium content in the irradiation volume to a level above the sensitivity limit of the activation method, and the postirradiation separation reduces the interference of other radioactivities.

Samples of natural water supplies were concentrated prior to activation by passing one liter aliquots through a column of hydrogen form Dowex 50W-X8 cation exchange resin. Elution of the vanadium was achieved with 2 *N* HNO_3. This procedure reduced the dissolved solids in the vanadium fraction by about fifty percent. The eluted samples were concentrated further by evaporation to volumes of 3 to 4 ml., and were quantitatively transferred to polyethylene irradiation vials. Repeated analyses of vanadium standards and blanks showed this preirradiation sample concentration procedure to be free of any detectable vanadium contamination from reagents or laboratory apparatus. Samples, standards, and reagent blanks were irradiated in the Stanford University 10 KW research reactor at a thermal neutron flux of about $10^{11} n \cdot cm^{-2} \cdot sec^{-1}$ for five minutes. The flux was measured in each irradiation by attaching pure, thin vanadium foils to the polyethylene vial.

Following irradiation, vanadium was extracted from the aqueous samples with oxine-chloroform solvent. The separation procedure involved immediate transfer of the irradiated sample into an Erlenmeyer flask containing 8 *N* NaOH and 330-day ^{49}V radiotracer used for chemical yield determination. The pH was adjusted to 4 with dilute HCl prior to extracting the vanadium into a one percent solution of oxine in chloroform. The vanadium was back extracted into an HNO_3-NH_4OH ammoniacal solution buffered to pH 9.4. The vanadium in the buffered phase was then washed with chloroform and transferred to a counting vial. The elapsed time between the end of irradiation and commencement of counting averaged six minutes.

Sample ^{52}V activities were measured with a 3 in. × 3 in. NaI(Tl) well-crystal detector coupled to a 400-channel gamma-ray spectrometer. In the time-sequence-store operational mode, the system stored integrated one minute counted activities of the 1.43 MeV photopeak in successive channels. These data of the photopeak activity, recorded at the end of each counting sequence with a teletype printer, provide a sensitive decay curve. The ^{52}V activity of the flux monitors was counted simultaneously with a second NaI(Tl) well crystal, and the photopeak was measured with a single channel analyzer. The sample activities were normalized for the specific activities of the monitor foils. Following decay of the 3.77 minute ^{52}V, the chemical yield was determined by liquid scintillation counting of the ^{49}V radiotracer.

Quantitative analysis of the vanadium in each sample was made by the comparator method, in which standard samples containing 10 μg of vanadium in demineralized water were irradiated for the same time period as the samples, and counted directly with no chemical separation. A flow diagram of the complete activation analysis procedure is presented in Figure 1.

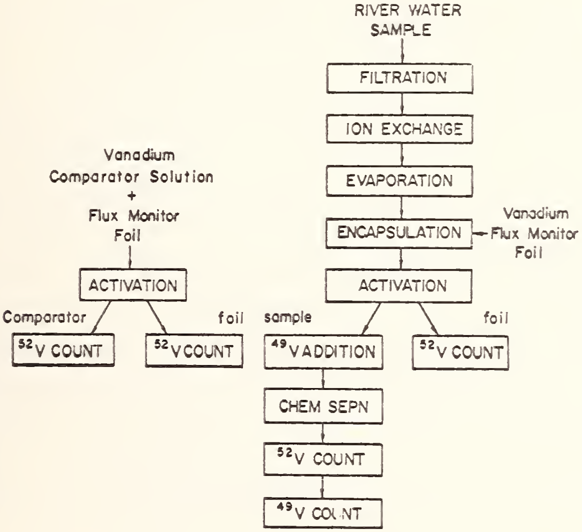

Figure 1. The procedure flow-sheet for neutron radioactivation analysis of vanadium in natural water with high concentration of dissolved solids.

For river waters, the major analytical interference was contributed by the gamma rays of 15 h ^{24}Na and 37.3 min ^{38}Cl. The effectiveness of the sample treatment procedures in reducing these interferences from typical Colorado River water is shown in the sequence of calculated relative activity spectra shown in Figure 2. Without chemical separation, the composite ^{24}Na-^{38}Cl activity represented by the upper curve in the first frame is approximately 150 times the vanadium activity in the vanadium photopeak channels. The ion exchange preirradiation concentration procedure eliminates the chlorine interferences from the sample. The interference spectrum due to the ^{24}Na is shown in the second frame. The ^{24}Na activity is still many times that of the vanadium activity. Following the postirradiation extraction, the vanadium photopeak activity makes the predominant contribution to the total activity in the photopeak channels as shown in the third frame. In the majority of the natural water analyses reported for which the vanadium concentration is about 3 μg/1, the sodium background contributes only 3-5% to the total activity extrapolated to the normalization time of five minutes after the end of irradiation. Correction for this contribution is made by subtracting the long-lived component of the decay curve.

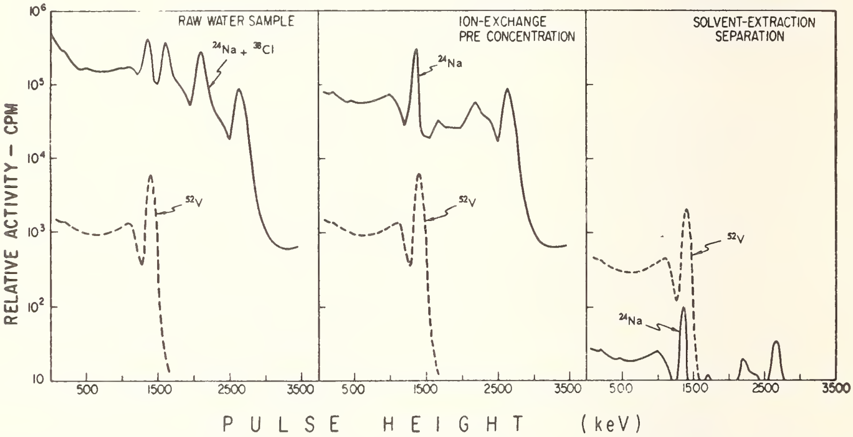

Figure 2. Improvement of the sensitivity for gamma-ray spectrometric measurement of ^{52}V with preirradiation concentration and post-irradiation radiochemical separations of vanadium in natural waters.

III. Results and Discussion

Initially, a series of standard sample was analyzed to assess the reproducibility of the activation analysis procedure for vanadium. These samples were prepared by adding vanadium as the vanadate in the presence of 200 mg/1 of NaCl in demineralized water. The NaCl provided 15 h ^{24}Na radioactivity interferences comparable to those encountered in the Colorado River samples. One liter samples containing 1.0 μg/1 of added vanadium were treated identically to the natural water samples. Table 1 summarizes the results of analyses of seven standard samples. The analyses yielded a mean vanadium concentration of 1.0 μg/1 with a standard deviation of ±10 percent.

This neutron activation analysis procedure was then applied to the analyses of 170 natural water samples. These samples were collected at 11 different sites throughout the Sacramento, San Joaquin, and Colorado River basins. A summary of the concentration data from these sites is presented in Table 2, which lists the range of concentrations observed at each site, as well as the mean concentration value for the samples analyzed. The vanadium concentrations in these natural waters ranged from a low value of 0.2 μg/1 to a high value of 49.2 μg/1. None of the

Table 1. Standard sample analyses.

Sample[a]	μg Vanadium added	μg Vanadium found
SD–10	1.0	1.3
SD–11	1.0	1.1
SD–12	1.0	1.0
SD–13	1.0	1.1
SD–14	1.0	0.9
SD–15	1.0	1.0
SD–16	1.0	0.8
Mean	1.0	1.0 ± 0.1

[a] 1 μg Vanadium Samples.

Table 2. Vanadium concentrations in natural waters (μg/l).

Sampling Site	Vanadium concentration range (μg/l)	Mean vanadium concentration (μg/l)
Sacramento River at Sacramento, California	3.44 – 4.31	3.93
San Joaquin River near Vernalis, California	6.75 – 7.01	6.87
Supply well in Fresno, California	19.4 – 21.6	20.5
Green River at Flaming Gorge, Utah	0.2 – 1.8	0.9
Animas River at Cedar Hill, N. M.	0.2 – 0.5	0.3
San Juan River Shiprock, N. M.	0.5 – 49.2	7.5
Colorado River near Loma, Colorado	1.9 – 11.5	4.6
Colorado River at Page, Arizona	1.5 – 5.2	3.4
Colorado River at Hoover Dam, Nevada – Arizona	1.8 – 4.1	3.0
Colorado River at Parker Dam, California – Arizona	1.7 – 4.3	3.0
Colorado River at Yuma, Arizona	1.0 – 3.8	2.2

samples analyzed had a concentration below the 0.1 μg/1 sensitivity limit of the method for one liter samples. On the basis of the data from the studies of analytical reproducibility, the standard deviations associated with these experimental values range between ±10% at 1.0 μg/1 concentrations and ±1% at 10 μg/1. The improvement in the analytical statistics with increased concentration is due primarily to the improved counting statistics associated with higher vanadium concentrations.

NEUTRON ACTIVATION ANALYSIS IDENTIFICATION OF THE SOURCE OF OIL POLLUTION OF WATERWAYS

V. P. Guinn and S. C. Bellanca

Gulf General Atomic Incorporated
San Diego, California

I. Introduction

In recent years, sharply increased attention is beginning to be devoted to the alarming problems of environmental pollution – pollution of air and pollution of water. This paper is concerned with a method of determining the origin (particular ship, pipeline, pier, or offshore well) of a given pollution event in which fresh water, brackish water or sea water is polluted – accidentally or intentionally – by heavy oil (crude oil or heavy fuel oil). An excellent summary of the nature and importance of the oil pollution problem is given in the publication, "Oil Pollution – a Report to the President" [1].

The method employed in this exploratory study was that of trace-element characterization *via* purely instrumental neutron activation analysis (NAA). In these exploratory measurements, 16 different marine fuel oils were analyzed by NAA, and their V, Mn, Na, Co, Sb, As, Cu, and Zn levels compared. The effects of prolonged contact with sea water and with fresh water upon these trace-element concentrations was also explored. As will be shown, the results were quite promising – indicating clearly the possibility of NAA trace-element characterization of oil-slick samples. A more comprehensive and more detailed study employing more recently developed Ge(Li) gamma-ray spectrometry and computer data handling techniques than were used in the exploratory study, is now being undertaken.

II. Experimental

A. SAMPLES

Samples of 16 different marine fuel oils and of the same 16 oils mixed with salty harbor water were supplied by an interested government agency.

B. SAMPLE PREPARATION

Before analysis, each sample was washed several times with hot deionized water to remove water-soluble dissolved and suspended matter in the oils and oil slicks, and to remove dissolved and suspended salts (from the salt water) from the oil-slick samples.

C. ANALYSIS

About 1 cm^3 of each sample to be analyzed was heat-sealed in a labeled half-dram polyethylene vial, weighed, and then activated for 15 seconds in the pneumatic-tube position of the 250 kW TRIGA Mark I reactor, where the thermal neutron flux is $4 \times 10^{12} n \cdot cm^{-2} \cdot sec^{-1}$. Each sample was counted shortly after irradiation, using a 3 inch × 3 inch solid NaI(Tl) crystal multichannel pulse-height analyzer. The principal induced activity detected following this short irradiation was 3.75-minute ^{52}V ($E_\gamma = 1.434$ MeV).

Later, groups of samples were activated for 30 minutes each in the rotary specimen rack of the reactor, where the thermal neutron flux is $2 \times 10^{12} n \cdot cm^{-2} \cdot sec^{-1}$. These samples were each counted as above, after a decay period of a few hours. The principal detected induced activities in these samples were 14.96 hour ^{24}Na ($E_\gamma = 1.369$ MeV and 2.754 MeV), and 2.576 hour ^{56}Mn [$E_\gamma = 0.847$ MeV (major), and 1.811 MeV and 2.110 MeV (minor)]. Some samples also showed the presence of 12.80 hour ^{64}Cu (0.511 MeV β^+ annihilation gamma ray), and in some, the presence of 13.8 hour ^{69m}Zn ($E_\gamma = 0.439$ MeV) was indicated. Most of the samples gave a small photopeak that corresponded to a mixture of the 0.559 MeV gamma ray of 26.4 hour ^{76}As and the 0.564 MeV gamma ray of 2.80 day ^{122}Sb. Since a Ge(Li) detector was not available at the time of the measurements and since only limited decay data were obtained, it was not possible to resolve this peak quantitatively into its ^{76}As and ^{122}Sb contributions.

The samples were also given a 9 hour irradiation in the rotary rack (flux $= 2 \times 10^{12}$ thermal $n \cdot cm^{-2} \cdot sec^{-1}$) and then counted after several days decay with a 3 inch × 3 inch well-type NaI(Tl) detector and multichannel pulse-height analyzer. From these measurements, the amount of cobalt in the samples was determined *via* the 2.505 MeV sum peak of 5.263 year ^{60}Co.

III. Results and Discussion

A. RESULTS

The V, Mn, Na, and Co values found for the 16 different fuel oils are shown in Table 1. The estimated standard deviations (1σ) based upon the counting statistics are not shown in the Table. However, the relative σ was, in general, only ± one or a few percent of the value for those values shown to three significant figures; ± about 5% for the values shown to two significant figures; and ± about 10% for those shown to only one significant figure. The values shown as less-than values are 3σ upper limits based upon the counting statistics in the region of the pulse-height spectrum where the particular photopeak should have appeared but actually was not detectable.

Table 1. Instrumental neutron activation analysis results on 16 different marine fuel oils.

	ppm Concentration Found			
Oil number	Vanadium	Manganese	Sodium	Cobalt
1	17.5	<0.30	35	0.92
2	175	0.043	7.9	0.39
3	220	0.020	1.69	0.62
4	470	0.077	44	0.41
5	77.6	<0.37	108	1.84
6	170	0.011	2.12	<0.07
7	3.8	0.002	0.36	0.08
8	865	<0.19	38	0.13
9	91	<0.39	25.0	0.40
10	250	<0.24	19.0	0.40
11	126	<0.23	7.0	0.23
12	284	0.08	12.4	0.25
13	292	<0.28	85	0.35
14	208	0.07	6.3	0.21
15	152	0.24	32	0.57
16	57.5	0.113	13.3	<0.08

It is seen that these various oil samples varied tremendously from one another in their vanadium contents: from as low as 3.8 parts per million (ppm) V to as high as 865 ppm V—a 228-fold range. Excluding the less-than values, the measured Mn values ranged from as low as 0.002 ppm Mn to as high as 0.24 ppm Mn—a 120-fold range. The sodium values ranged from as low as 0.36 ppm Na to as high as 108 ppm Na—a 300-fold range. The range of cobalt concentrations was less: 23-fold, ranging from as low as 0.08 ppm Co to as high as 1.84 ppm Co.

Even if one allows a ±10% uncertainty in each value shown in Table 1, it is found that no two oils of the 16 analyzed are sufficiently similar—in concentrations of these four elements—that they cannot be distinguished from one another. However, the levels of all four elements are needed in some instances to distinguish one oil from another unambiguously. Additional points of comparison would be desirable, particularly if one is considering a much larger population of oils of different origins.

Since oil-slick samples recovered from salt water may be appreciably contaminated from the salt water, they need to be washed clean first. In order to ascertain whether water washing modifies the trace-element concentrations in such oil samples appreciably, 8 of the 16 samples were analyzed as received, and after being washed several times with hot deionized water. The V, Mn, and Co levels generally were not appreciably changed by the washing (average change due to washing: +12%, −9%, and −4%, respectively, but the Na levels (not surprisingly) were decreased by an average of 34%.

Also, samples of the original 16 fuel oils, and of the same oils that had been in contact with salty harbor water for several weeks were each washed several times with hot de-ionized water, then analyzed as before. The water-washing procedure appeared to remove from the oil, salts that came from the salt-water reasonably well with the exception of sodium. Thus, the V, Mn, and Co levels of the oils that had been in contact with salt water after water-washing averaged 5% lower, 10% higher, and 8% higher, repectively, than the corresponding water-washed oils that had not been in contact with salt water. However, the sodium levels averaged 18% higher.

B. Discussion

The results described, although limited in scope and depth, certainly indicate that high-flux instrumental thermal NAA [2,3] offers definite promise for the trace-element-characterization matching of an actual oil-slick sample with one sample of fuel oil—out of a number of suspect samples. The broader and deeper study now being initiated should establish this possibility more rigorously and provide a mathematical basis for the interpretation of results obtained on oil and oil-slick samples obtained by enforcement agencies in the investigation of individual violations of oil pollution laws. The various characterizing trace elements, occurring in the original crude oils largely as essentially non-volatile metal porphyrins, remain in the residue left when the volatile components of the crude evaporate (as from an oil slick), and when the light ends are distilled off in refining. Thus, NAA matching of the levels of these trace elements—between an oil-slick and its polluting source—may, for the first time, provide a method of identification of the source of oil pollution of waters that will aid in the enforcement of present oil pollution laws.

IV. Acknowledgment

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Energy Commission (Contract AT(04-3)-167, Project Agreement No. 15).

V. References

[1] "Oil Pollution—a Report to the President (a Report on Pollution of the Nation's Waters by Oil and Other Hazardous Substances)", by the Secretary of the Interior and the Secretary of Transportation, February, 1968 (Sup't. of Documents, U.S. Gov't. Printing Office, Washington, D. C.).

[2] Guinn, V. P., and Wagner, C. D., Anal. Chem. **32,** 317 (1960).

[3] Guinn, V. P., Johnson, R. A., and Mull, G. C., Proceedings of the Sixth World Petroleum Congress (Frankfurt, Germany, 1963), p. 162.

CHAPTER 2

BIOMEDICAL APPLICATIONS

Synopsis of Discussions

DOMINIQUE COMAR, *Chairman*

C.E.A.
Departement de Biologie
Service hospitalier Frederic Joliot
91—France

The first of these two sessions on biomedical applications of neutron activation analysis has been mainly concerned with the analysis of human and animal tissues. It is important to point out that biologists and medical people are not the last to use the technical improvements that chemists and physicists have worked out. May I just indicate that among the 21 papers concerned in this symposium with the use of Ge(Li) detectors for analytical purposes, one third are related to biomedical problems. In the case of multielement analysis of tissues by a purely instrumental method, it has been asked if the stainless steel knives that are used to prepare the samples could not be a source of contamination. The answer was "no".

Some new methods coming from chemists have been used for rapid chemical separation for copper and manganese measurements in brain tissue.

Single element techniques with chemical separation has also been described, for example, in the determination of tellurium in human tissue. This practical method leading to high purity compounds and high sensitivity detection would certainly be a good method for people interested in tellurium metabolism. It was pointed out that the presence of uranium in the sample could give false results.

In the field of the use of neutron activation analysis for the study of biological problems, two aspects are illustrated by the work reported in this session.

First: Methods which can be directly used for diagnosis of disease. It must be said that until now except in a few cases, this goal of activation analysis has not been very satisfactory, mainly because if the determination of an element in a biological sample can help in the diagnosis, it has to be demonstrated first that this element has an essential role. For some of these such as copper, zinc, or iodine, other competitive methods often are easier to perform. But in the case of very small samples in which nondestructive analysis can be carried out to measure known essential elements such as sodium or chlorine, neutron activation analysis is a very useful technique. This has been demonstrated by the group from Texas and the group from Seattle in their work on sodium concentration in nail as a test for diagnosis of cystic fibrosis. The feasibility of this method in the future is in question. Complicating the problem is the preparation of the sample, since we know that the amount of sodium in the nail varies with *in vivo* washing in infants and varies with the age of the patient.

The second goal of neutrol activation analysis which has been studied is well represented by the work of the Battelle Memorial Institute group from Richland, the Massachusetts General Hospital group from Boston and the Rochester group. Their interest is to know the "normal" trace element composition of tissues and then to look for variations caused by diseases such as cancer or atherosclerosis. A number of hypotheses support such work. For example, a correlation between the hardness of drinking water and long-life has been reported. With respect to the relationship between trace elements and cancer, I want to recall the hypothesis put forward by Warburg in 1956. He claimed that the growth of tumors is associated with the alteration of metabolism from aerobic to anaerobic. It is known that the enzymes which control this process are metalloenzymes. Therefore, it is possible that a change in the trace element concentration in tissues resulting in inactivation of the enzymes may alter metabolism.

Regarding the future development of activation analysis, it was stated that this technique had been accepted more in the medical than in the industrial field. There are only a very few reactors in hospitals now, but the development of compact cyclotrons which can be used to prepare short-lived radioisotopes of medical interest may contribute to the extension of activation analysis in hospitals.

The second session covered a number of diversified areas and materials: radioecology, analysis of animal diets, plant tissues, wine, and tobacco. Also discussed were irradiation facilities for biological samples and measurements of high sensitivity to test the specific activity of radioisotopes.

The same kind of technical discussions took place with regard to destructive and nondestructive analysis as those during the first biomedical session. The matrix, animal tissue, is not very different from plant material, but the elemental ratios change. For high sensitivities which are required in radioecological studies, techniques using chemical separation with sodium iodide spectrometry seems preferable to the nondestructive methods. Although chemical separations may be totally or partly automated, they may be time consuming. Instrumental analysis using Ge(Li) detectors allows one to measure fifteen elements simultaneously in the same sample, but some of those elements with photopeaks on the Compton background of a higher energy gamma ray will only be detected with low sensitivity and poor accuracy. If we use only instrumental analysis we will miss elements of biological interest.

In order to increase the sensitivity, the Washington State University group irradiate samples of 5 to 10 grams, but they are aware of the inhomogeneity of neutron flux during irradiation of such large samples. It appears to us that there will be a compromise between the two approaches, chemical and instrumental analysis.

Many biological problems were reported. The Grenoble group discussed activation analysis for tracer experiments which led to interesting results concerning the contamination of the biosphere with radioactive wastes. The Food and Drug Administration group from Washington, D.C. has obtained good results by preparing a food with very low vanadium content for animals. With regard to trace element content in the diet it would be of interest to know the concentration at which a diet may be considered deficient when the elements concerned have not been proven essential. As an example, a diet containing less than 20 ppb of iodine is deficient because when given to rats it induces goiter. There is a need for people working in trace mineral metabolism to obtain the very lowest concentration of the element concerned in the diet in order to prove that it is essential. By this means cobalt was proven to be an essential element for man and animals. If activation analysis is the most sensitive technique for element measurement, it should be used in the preparation of these diets. It was also pointed out that it is important to know the trace element concentration in the contaminated air we are inhaling that results from tobacco smoke and in the wine we drink. This represents the opposite situation to a deficiency in trace elements and is related to the toxicological approach.

THE MULTIELEMENT ANALYSIS OF BIOLOGICAL MATERIAL BY NEUTRON ACTIVATION AND DIRECT INSTRUMENTAL TECHNIQUES[1]

Louis A. Rancitelli, John A. Cooper and Richard W. Perkins

Battelle Memorial Institute
Pacific Northwest Laboratory
Richland, Washington 99352

I. Introduction

Although several studies concerning the trace element concentrations in biological organisms have been conducted over the years [1], the roles of most trace elements in biological processes remain poorly understood. This situation can in part be attributed to the lack of suitable analytical technology which will permit precise multielement analysis in the parts per million to sub-parts per billion range. Two analytical techniques, emission spectroscopy [2], and spark source mass spectrometry [3] have been shown to be capable of simultaneous multielement analysis of biological material. However, these methods require extensive sample preparation with its associated contamination problems, and are seriously limited in sensitivity for many trace constituents by matrix effects and spectral interferences. The extension of trace element measurements to permit an analysis of the fine structure of the body organs and of cellular areas within the organs requires even greater care in sample acquisition, sample preparation and analysis together with a very sensitive analytical method.

A great deal can be learned regarding the metabolic role of a trace element having a known biological function. Also, from the large elemental variations which have been observed within an organism [4], it is evident that the concentration of the intra-related trace elements should be simultaneously measured.

Neutron activation analysis has provided a practical means of solving many environmental and biomedical problems which require trace element sensitivities beyond the capability of other techniques. Previous work has been mainly concerned with the instrumental determination of a few specific elements or extensive multielement determinations involving radiochemical separations prior to gamma-ray analysis [5].

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[1] This paper is based on work performed under United States Atomic Energy Commission Contract AT(45-1)1830.

The objectives of this work have been to develop and apply comparative methods of neutron activation analysis which permit the direct instrumental measurement of some 20 trace elements in biological materials. These include a large number of the biologically important elements together with several elements which have unknown biological functions. The method involves a minimum of preirradiation handling, requiring only that the sample be freeze dried prior to neutron irradiation.

II. Experimental

A. Apparatus and Reagents

Two irradiation facilities were employed in this investigation. The first, the heavy water moderated Plutonium Recycle Test Reactor (PRTR), has a rabbit system with a delivery time of about 10 seconds, and a neutron flux of about $2 \times 10^{13} n \cdot cm^{-2} \cdot sec^{-1}$ with a cadmium ratio in excess of 100. The second facility was a graphite moderated Hanford Production Reactor with its characteristic high, well thermalized neutron flux.

The gamma-ray spectrometric analysis of neutron activated samples was performed with two detector systems. The first consisted of a high resolution five-sided coaxial Ge(Li) detector with an active volume of 20 cm^3 [6]. The second detector system was an anticoincidence shielded, gamma-gamma coincidence multidimensional analyzer employing NaI(Tl) crystals [7].

Preirradiation sample preparations were performed in an Agnew-Higgins laminar flow work station. All biological samples were dissected with clean carbon steel scalpels, placed directly in polyethylene capsules which had been cleaned with nitric acid, and dried in a Thermovac Industries Freeze Drier. This sampling procedure was shown to result in a negligible transfer of contamination to the sample [8].

Standard solutions were prepared from Mathey Spec Pure materials dissolved in redistilled nitric acid and diluted with double distilled water. The neutron flux monitors consisted of high purity cellulose [9] on which known amounts of the standard solutions had been dried or 100 microliter aliquots of dilute (10^{-6}g/ml – 10^{-8}g/ml) solutions of each element of interest sealed in 3 mm i.d. quartz ampoules.

B. Procedure

The samples and standards were first irradiated in tandem in the rabbit facility of the PRTR reactor to an integrated thermal neutron exposure of $2 \times 10^{15} n/cm^2$. The polyethylene irradiation containers were then vented to eliminate ^{41}Ar, and placed in a standard counting geometry above the Ge(Li) detector. Gamma-ray spectra of the activated samples and standards were obtained after appropriate decay intervals to determine the neutron induced activities of ^{24}Na, ^{27}Mg, ^{38}Cl, ^{42}K, ^{80}Br, and in the case of lung tissue, ^{28}Al. Typical gamma-ray spectra of neutron activated beef and fish muscle are presented in Figures 1 and 2.

Following a one week decay, the samples and a set of standards sealed in quartz ampoules were reirradiated with an integrated thermal neutron exposure of 7×10^{17}n/cm^2. After a decay interval of two days, the samples were pulverized, suspended in a 2% agar solution (contained in 1/2 in. × 2 in. rings to provide a standard counting geometry) and counted on a Ge(Li) spectrometer along with appropriate standards to permit the determination of Na, K and Br from their neutron activation products ^{24}Na, ^{42}K, and ^{82}Br. After a decay interval of about twenty days, a second Ge(Li) gamma-ray spectrum revealed the characteristic photopeaks of ^{51}Cr, ^{59}Fe, ^{60}Co, ^{65}Zn, ^{75}Se, ^{86}Rb, ^{134}Cs, and ^{203}Hg. In the case of some human lung tissue samples, ^{46}Sc, ^{124}Sb, and ^{233}Pa were also observed, and in spectra taken about 10 to 15 days after irradiation, ^{198}Au and ^{239}Np were present. The initial identification of each photopeak was based on measurements of energy, relative spectral intensity and half life. It was necessary to strip the component of ^{75}Se from the 279 keV photopeak of ^{203}Hg prior to calculating the concentration of mercury. All other photopeaks employed in the analysis were found to be free of spectral interferences.

A third set of gamma-ray spectra of the sample and standards was obtained with the gamma-gamma coincidence multidimensional analyzer about 45 days after irradiation and from these, the parent elements of the observed radionuclides ^{46}Sc, ^{60}Co, ^{65}Zn, ^{110m}Ag, ^{124}Sb, and ^{134}Cs, were determined.

III. Results and Discussion

A. Results

The accuracy and precision of this instrumental method of analysis was estimated by analyzing high purity cellulose samples to which known amounts of each element of interest had been added. The average measured concentrations of trace elements in three samples of this material and the standard deviation of the average [10] are compared with actual concentrations in Table 1. The observed average concentrations compare quite well with the actual concentrations except for Ag and Sc. The agreement is within the errors associated with counting statistics plus the estimated experimental error associated with sample self-shielding, contamination, flux gradients and interfering nuclear reactions [8].

Several types of biological material, high purity cellulose air filters, human lung tissue, beef muscle, and fish muscle are being analyzed by

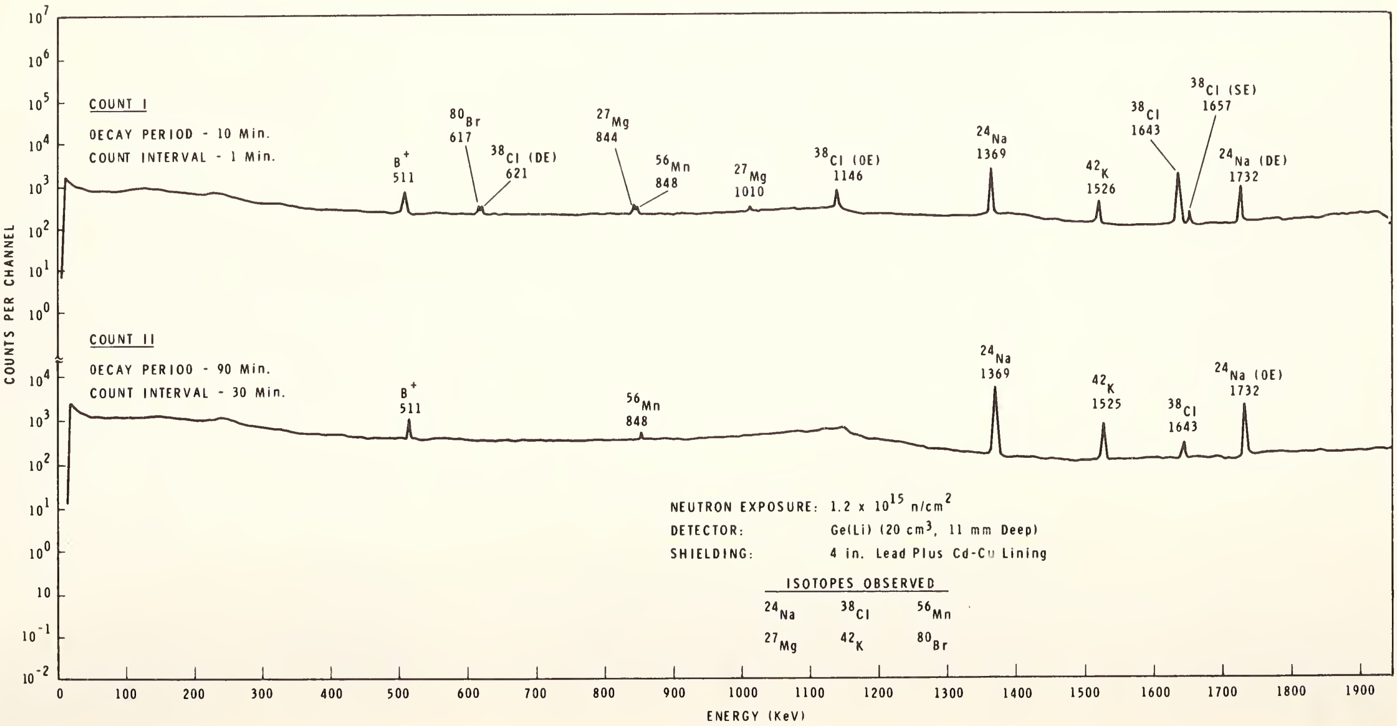

Figure 1. Gamma spectra of neutron activated beef muscle.

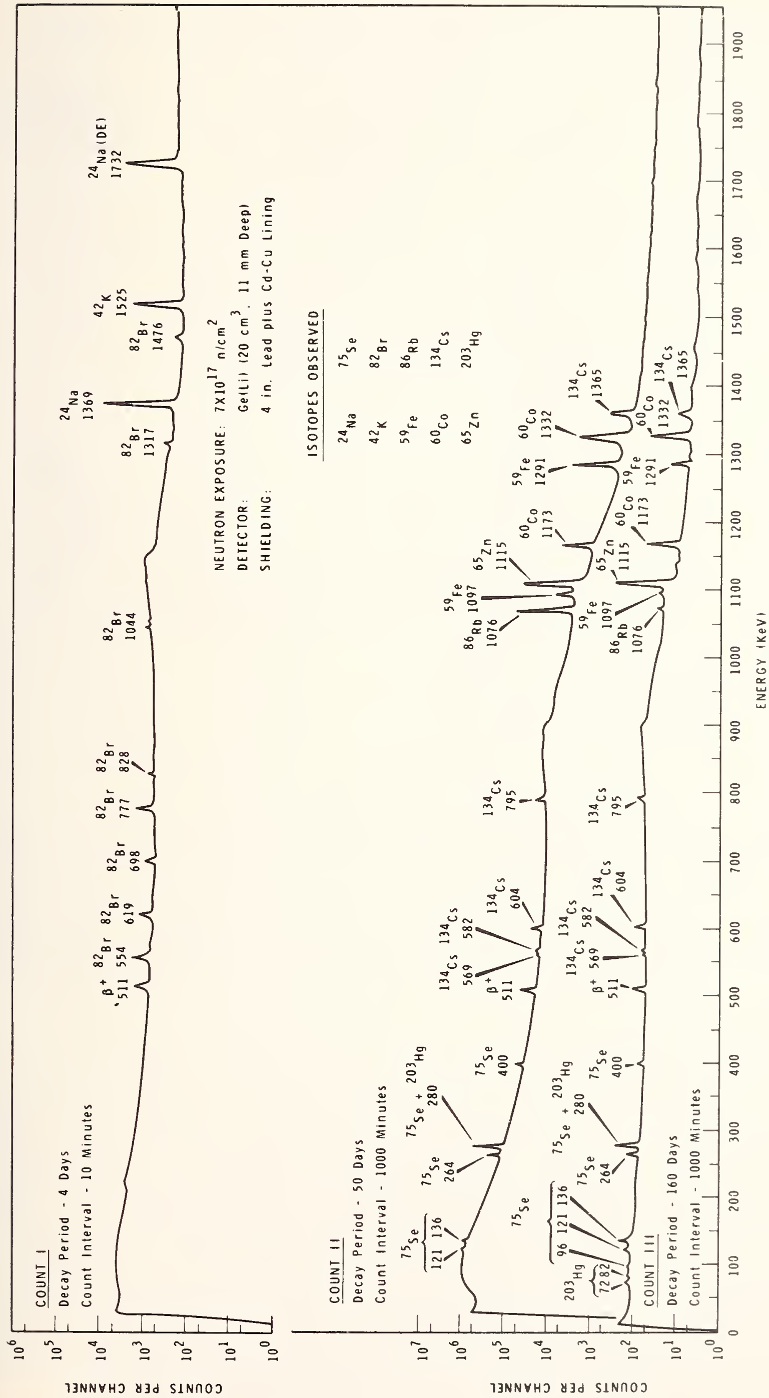

Figure 2. Gamma spectra of neutron activated fish muscle.

Table 1. Results of the analysis of synthetic biological samples by neutron activation.[a]

Element	Actual concentration	Average ± σ [b]	Estimated experimental error percent
Sodium	1,700	1,770 ± 60	5
Potassium	20,000	20,400 ± 700	5
Rubidium	6.6	6.5 ± 0.6	5
Cesium	0.104	0.103 ± 0.006	5
Bromine	10.8	10.8 ± 0.6	5
Zinc	83.4	87 ± 3	10
Iron	33.2	33 ± 3	5
Cobalt	0.064	0.065 ± 0.006	10
Selenium	0.44	0.41 ± 0.03	15
Mercury	0.52	0.49 ± 0.02	10
Chromium	1.2	1.3 ± 0.2	10
Silver	0.014	0.012 ± 0.003	10
Antimony	0.026	0.027 ± 0.001	10
Scandium	0.010	0.012 ± 0.001	5

[a] Micrograms per gram of dry tissue.

[b] Average of three determinations.

this technique in a variety of environmental and biological programs and a few examples which demonstrate the applicability of the method are included. The results of the analyses of some of these materials are presented in Table 2 with the standard deviation of each average (where replicate analyses were performed) and the total estimated experimental error.

The value of the simultaneous measurement of the concentrations of several elements in a single sample of tissue is demonstrated from our study of the variation of cesium and rubidium in an organism relative to potassium. The ratios of rubidium and cesium to potassium in various types of muscle tissue of a silver salmon are presented in Table 3 together with the ratios reported in sea water. This observation suggests that while rubidium and potassium are taken up by this organism in direct proportion to their concentration in sea water, the organism has the ability to differentiate and accumulate cesium relative to potassium. Concentration factors of 3 to 8 in the cesium to potassium ratio of the organism relative to the ratio in sea water are not explained by simple diffusion since the hydrated ionic radius of Cs, Rb and K are quite similar [11].

Table 2. Trace element concentrations of biological materials as determined by neutron activation analysis.[a]

Element	IPC filter (cellulose)	Human lung tissue	Beef muscle	Silver salmon muscle, dorsal	Trout muscle, dorsal	Estimated experimental error percent
Potassium	< 20	6300	11,400 ± 200	16,800 ± 100	18,900 ± 1100	5
Chlorine	38 ± 3	11,000	1430 ± 60	- - - - - - -	- - - - - - -	5
Sodium	72 ± 2	9000	1730 ± 120	920 ± 30	600 ± 20	5
Magnesium	- - - - - - -	- - -	550 ± 40	- - - - - - -	- - - - - - -	5
Iron	5.7 ± 0.1	430	91 ± 7	7.6 ± 0.6	9.2 ± 0.7	10
Aluminum	4.6 ± 0.4	190	< 10	- - - - - - -	- - - - - - -	5-20
Zinc	0.64 ± 0.03	55	170 ± 10	12 ± 1	11.5 ± 0.5	5
Bromine	0.16 ± 0.02	15	11.9 ± 0.9	26 ± 2	10.5 ± 0.5	5
Rubidium	- - - - - - -	10.4	4.2 ± 0.2	5.6 ± 0.1	16.6 ± 0.1	5
Selenium	- - - - - - -	1.1	0.18 ± 0.003	0.96 ± 0.02	0.67 ± 0.03	10
Chromium	0.13 ± 0.06	1.1	0.04 ± 0.02	< 0.02	0.12 ± 0.05	5-15
Manganese	1.2 ± 0.1	- - -	0.31 ± 0.02	- - - - - - -	- - - - - - -	5
Mercury	- - - - - - -	0.14	< 0.10	0.30 ± 0.05	0.39 ± 0.01	15
Cobalt	0.0026 ± 0.0001	0.092	0.014 ± 0.001	0.0055 ± 0.0005	0.011 ± 0.0005	5
Cesium	0.0003 ± 0.00004	0.041	0.010 ± 0.001	0.105 ± 0.005	0.110 ± 0.004	5
Antimony	0.0015 ± 0.0002	0.070	0.0006 ± 0.0001	0.0001	0.0004 ± 0.0002	5-20
Gold	- - - - - - -	0.040	- - - - - - -	- - - - - - -	- - - - - - -	10
Silver	< 0.001	0.019	< 0.001	0.001	0.0014 ± 0.0002	5-20
Scandium	0.00040 ± 0.00001	0.021	0.00056 ± 0.00007	0.00003 ± 0.00001	0.00004 ± 0.00001	5-50
Number of analyses	5	1	3	2	2	

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[a] Micrograms per gram of dry tissue.

Table 3. Relative concentrations of cesium, potassium, and rubidium in silver salmon tissue.

	Relative concentration	
	Rubidium/potassium ($\times 10^4$)	Cesium/potassium ($\times 10^6$)
Red muscle	3.6 ± 0.2	6.8 ± 0.1
White muscle	3.4 ± 0.1	6.2 ± 0.3
Cheek muscle	4.0 ± 0.3	5.8 ± 0.2
Liver	3.8 ± 0.6	2.5 ± 0.5
Sea water [12, 13]	3.3	0.8

B. DISCUSSION

The direct instrumental neutron activation analysis of biological material employing both Ge(Li) gamma-ray spectrometry and NaI(Tl) gamma-gamma coincidence multidimensional spectrometry has been shown to be a sensitive, accurate and precise method of trace element analysis. The versatility of the method permits the determination of some 20 elements in a single sample of dry tissue without resorting to chemical separations. The method is currently being employed to study a variety of environmental and biomedical problems including the trace element distribution through the organs and muscle in terrestrial, aquatic and marine organisms and in man.

IV. References

[1] Bowen, H. J. M., Trace Elements in Biochemistry, Academic Press, New York (1966).

[2] Bedrosian, A. J., Skogerboe, R. K., and Morrison, G. H., Anal. Chem. **40,** 854 (1968).

[3] Evans, C. A., and Morrison, G. H., Anal. Chem. **40,** 869 (1968).

[4] Rancitelli, Louis A., Haller, W. A., and Cooper, J. A., Pacific Northwest Laboratory Annual Report for 1967 in the Physical Sciences to the USAEC Division of Biology and Medicine, in press.

[5] Samsahl, K., Wester, P. O., and Landstrom, O., Anal. Chem. **40,** 181 (1968).

[6] Cooper, J. A., Wogman, N. A., Palmer, H. E., and Perkins, R. W., "The Application of Solid State Detectors to Evironmental and Biological Problems," to be published in Health Physics, 1968.

[7] Perkins, R. W., and Robertson, D. E., "Selective and Sensitive Analysis of Activation Products by Multidimensional Gamma-Ray Spectrometry," Proceedings of the International Conference: Modern Trends in Activation Analysis, College Station, Texas, April 19-22, 1965. Conf. 650405, pp. 48-57, Division of Technical Information Extension, USAEC.

[8] Rancitelli, L. A., Haller, W. A., and Cooper, J. A., Pacific Northwest Laboratory Annual Report for 1967 in the Physical Sciences to the USAEC Division of Biology and Medicine, in press.

[9] Rancitelli, L. A., Tanner, T. M., and Haller, W. A., A High Purity Cellulose As a Possible Biological Reference Material, The 1968 International Conference, Modern Trends in Activation Analysis, Gaithersburg, Maryland, (October 7-11, 1968).

[10] Friedlander, G., Kennedy, J. W., and Miller, J. M., Nuclear and Radiochemistry, John Wiley and Son, Inc., New York, 1966, p. 168.

[11] Wilde, W. S., in Mineral Metabolism, Vol. 2, Part B, C. L. Comar and F. Bronner, Eds., Academic Press, New York, 1962, p. 74.

[12] Bolton, E., Turekian, K. K., Schutz, D. F., Geochim. et Cosmochim. Acta **28**, 1459 (1964).

[13] Fabricand, B. P., Imbimbo, E. S., and Brey, M. E., Deep Sea Research **17**, 785 (1967).

MULTIELEMENT ANALYSIS OF PATHOLOGICAL TISSUE

**D. M. Linekin, J. F. Balcius,
R. D. Cooper and G. L. Brownell**

*Massachusetts General Hospital and
U.S. Army Natick Laboratories
Boston, Massachusetts*

I. Introduction

In recent years information has accumulated concerning the relationship existing between abnormal trace element levels in the body and certain pathological conditions. Schroeder, who has been a major contributor to this field, finds evidence that a deficiency of chromium may be associated with the onset of diabetes and that an excess of cadmium may be linked to essential hypertension [1]. Cotzias has noted the existence of relationships between the metabolism of manganese and various aspects of health and disease [2]. Pories and Strain have studied the relationship between zinc deficiency and atherosclerosis [3]. At the Symposium on Nuclear Activation Techniques in the Life Sciences in Amsterdam in May of 1967 several papers were presented linking abnormal trace element levels with a variety of disorders [4]. It appears that a better understanding of many diseases will result from more knowledge of the trace element content in various organs and components of biological systems in different disease states.

It is fortunate that activation analysis is well suited to the determination of minute quantities of many of the trace elements which are of the greatest biological significance. This paper describes a nuclear activation technique which permits the simultaneous measurement of several trace elements in biological tissue. Some recent results of trace element measurements in certain pathological tissues are also presented.

II. Experimental

A technique has been developed for the simultaneous measurement of several trace elements in various biological systems [5]. This technique combines activation with thermal neutrons, detection by means of a large 35 cm^3 coaxial Ge(Li) detector, and data analysis by computer. The method is purely instrumental, involving no chemical separation. The detector resolution of less than five keV is such that the ^{86}Rb 1.079 MeV, the ^{59}Fe 1.100 MeV, and the ^{65}Zn 1.119 MeV photopeaks can be completely resolved.

The methods of procedure for these studies may be divided into the following stages: sample preparation, activation, detection, data recording, and data processing. Great care is taken to minimize contamination and treatment of the samples before irradiation. Six biological samples are individually sealed in clean polyethylene vials and are irradiated in the M.I.T. 5 MW research reactor in a flux of 2×10^{13} thermal neutrons per cm^2 per sec for a period of nine hours. A specially prepared chemical standard containing accurately measured amounts of several trace elements is simultaneously irradiated. After about nine days, during which the excessive amounts of ^{24}Na and ^{42}K decay, the activated samples and standard are transferred to counting vials and are analyzed in the Ge(Li) spectrometer for times between 400 and 1000 minutes. Each gamma-ray spectrum is recorded by a point plotter by an Optikon readout unit, and on paper tape. The data are then computer processed, the comparator method being used to yield the desired trace element concentrations.

The chemical standard consists of twelve elements distributed homogeneously in a cellulose matrix. It is prepared by lyophilizing a solution containing appropriate amounts of each component. The elements; Sn, Hg, Cd, Cr, Au, Sb, Br, Ag, Rb, Fe, Zn, and Co, are present in most biological samples and have thermal neutron produced isotopes of long half life. The amount of each element in the standard (ranging from 0.04 μg of Au to 860 μg of Fe in 20 mg of cellulose powder) is chosen so that good statistics will be obtained in each photopeak in a 100 minute count 10 days after irradiation. The cellulose has somewhat the same density as that of biological tissue. Therefore, the standard is a close approximation to a typical biological sample in terms of thermal neutron absorption and gamma ray self-absorption properties.

The computer method used in these studies has been adapted from a method developed by Inouye and Rasmussen [6] for the analysis of complex gamma-ray spectra. The main feature of this approach is a data smoothing technique employing a Fourier transform. The raw data is transformed into "energy frequency" space, multiplied by a suitable filter function, and then transformed back to energy space. The resulting smoothed data contains most of the information in the original data, but random fluctuations have been eliminated. The background, which is determined by connecting the minima of the smoothed spectrum, is then subtracted to obtain the spectral peaks. Peak energies are determined by a zero slope criterion, and peak areas are determined by summing all the counts between successive zeros in the background-subtracted data.

Corrections are made for counting time, decay time, and mass or volume of the unknown sample and the results are expressed in terms of μg of trace element per gram of wet tissue or per ml of blood.

III. Results and Discussion

The trace element content of the lung of a man who died of lung disease resembling asbestosis or silicosis was compared with a normal lung. It was found that the bromine and zinc concentrations in the fibrotic parenchyma were greater than in the normal parenchyma whereas the rubidium and iron concentrations were less. The mercury, chromium, bromine, rubidium, iron, and cobalt concentrations were less in the fibrotic pleura than in the normal pleura but the zinc concentration was greater.

Measurements of trace element levels in the blood, heart, and diaphragm of a Syrian golden hamster with a dystrophy-like myopathy have been made. These levels have been compared with similar measurements on a control hamster. The only striking differences observed were an increase in the zinc and cobalt concentrations in the dystrophic heart and a decrease in the zinc concentration in the dystrophic blood.

In Table 1 the results of trace element measurements in two types of experimental mouse tumors are presented. Four rhabdomyosarcomas and three mammary adenocarcinomas were studied. It appears that the chromium and iron concentrations are greater in the rhabdomyosarcomas.

Table 1. Trace element content of experimental mouse tumors in μg/g wet tissue.

	Rhabdomyosarcoma				Mammary adenocarcinoma		
Element	1	2	3	4	1	2	3
Chromium		1.5	1.3				.28
Bromine	6.0	6.7	6.2	6.0	10.0	6.4	7.0
Rubidium	4.4	1.3	1.9	3.4	7.3	3.5	1.9
Iron	114	69	54	146	42.0	30.8	9.0
Zinc	16.5	8.4	12.3	15.1	21.9	14.2	5.8

The range of values shown here is typical of what we have obtained in our preliminary measurements in pathological tissue of this type. Naturally, before any definite conclusions may be made, a thorough study must be carried out.

IV. References

[1] Schroeder, H. A., J. Chron. Dis. **18,** 217-228 (1965).
[2] Cotzias, G. C., Physiol. Revs. **38,** 503-532 (1958).
[3] Pories, W. J., Rob, C. G., Smith, J. D., Henzel, J. H., and Strain, W. H., Proc. 7th Int. Cong. Geront., 449, Vienna (1966).
[4] Proceedings of the Symposium on Nuclear Activation Techniques in the Life Sciences held in Amsterdam, 8-12 May, 1967, International Atomic Energy Agency, Vienna, 1967.
[5] Cooper, R. D., Linekin, D. M., and Brownell, G. L., Proceedings of the Symposium on Nuclear Activation Techniques in the Life Sciences held in Amsterdam, 8-12 May, 1967, pp. 65-80.
[6] Inouye, T., and Rasmussen, N. C., Trans. Am. Nucl, Soc. **10,** 38 (1967).

THE USE OF NEUTRON CAPTURE GAMMA RADIATIONS FOR THE ANALYSIS OF BIOLOGICAL SAMPLES

D. Comar, C. Crouzel, M. Chasteland,
R. Riviere and C. Kellershohn

Atomic Energy Commission
Department of Biology
Frederic Joliot Hospital
91-Orsay, France

I. Introduction

The method of analysis by which capture gamma rays are detected during neutron or charged particle irradiation is difficult to put into practice because of the size of the equipment required, *e.g.* nuclear reactors or cyclotrons. Very little work has appeared which describes the application of this method, involving the capture of either neutrons [1-4] or charged particles [5], while to our knowledge no work has been carried out on the capture gamma rays resulting from thermal neutron irradiation of biological products. However Newton *et al* [6] have shown the 2.23 MeV neutron capture gamma-ray line of hydrogen on gamma-ray spectra obtained with a whole body counter when measuring the radioactivity of normal subjects. Initially the neutrons were produced by the interaction of cosmic radiation with the shielding of the measurement chamber; later the phenomenon was intensified by the use of a radium-beryllium source. We shall discuss our first results obtained during neutron irradiation of various biological products, both *in vitro* and *in vivo*.

II. Preliminary Considerations

The total number of impulses produced by a detector during the complete disintegration of a radionuclide produced by irradiation of an element is given by the standard relationship:

$$n=\frac{WN}{A}\Phi\sigma\theta\epsilon f\frac{1-e^{-\lambda t}}{\lambda} \qquad (1)$$

where n is the total number of impulses produced at the level of the spectral peak chosen, W the total mass of the element under investigation in the irradiated sample, A the atomic weight of the element, N Avogadro's number, Φ the particle flux, σ and θ respectively the cross section and the isotopic abundance of the isotope used, ϵ the total efficiency of the detector for the photons corresponding to the spectral peak chosen, f the number of photons emitted by disintegration, λ the radioactive constant of the radioelement formed, and t the irradiation time.

On the other hand the total number of impulses due to capture gamma rays during irradiation of the same sample in the same flux is given by:

$$n' = \frac{WN}{A} \Phi \sigma' \theta' \epsilon' f' t' \tag{2}$$

the symbols represent the same quantities as in equation (1) but the "prime" sign attached to them means that these quantities assume a different value.

We can then write:

$$\frac{n'}{n} = \frac{\sigma' \theta' \epsilon' f' t'}{\sigma \theta \epsilon f \dfrac{1 - e^{-\lambda t}}{\lambda}} \tag{3}$$

Theoretically the advantages of the capture gamma ray method lie in the following four points: (1) Time t' can be as long as desired, whereas time $\dfrac{1 - e^{-\lambda t}}{\lambda}$ is limited to the value $\dfrac{1}{\lambda}$. (2) Very often the stable isotopes that are most abundant in the natural element and which frequently have the highest cross sections, are unsuitable for radioactivation analysis because the (n,γ) reaction transforms them into another stable isotope of the element in question or into a long-lived radioisotope of low activity. Nevertheless these isotopes provide utilizable capture gamma rays during the irradiation. The behavior of biologically interesting elements such as H, N and B is exemplary in this respect. (3) The number f' of capture photons emitted for each nuclear reaction is of the same order of magnitude as f. (4) For certain elements such as phosphorus and sulfur, pure beta-ray emitters are produced, and therefore, nondestructive analysis is not possible by neutron radioactivation; whereas it can still be carried out by capture gamma-ray determination.

To illustrate the first three points let us consider the case of chlorine. Neutron activation analysis can only make use of chlorine-37, the measurement being made on the 1.64 MeV total absorption peak of chlorine-38. Under these conditions we have: $\sigma = 0.435$ b, $\theta = 0.245$ and $f = 0.31$. For the capture gamma-ray determination on the other hand both chlorine-35 and chlorine-37 can be used, and by performing the measurement on the absorption peak corresponding to the 6.11 MeV capture photons which represent the strongest line of the high energy capture spectrum, we have: $\sigma' = 33.2$ b, $\theta' = 1$ and $f' = 0.25$, whence:

$$\frac{\sigma'\theta' f'}{\sigma\theta f} = 251. \tag{4}$$

Thus if in the two methods, capture and radioactivation, the backgrounds and the efficiencies ϵ' and ϵ of the detectors used were the same, the analysis by capture gamma-ray determination would be much the better. Unfortunately in order to separate properly the many capture gamma-ray lines, it is desirable to use a detector such as a lithium compensated germanium detector, which has a very good resolution but is considerably less efficient than the scintillation detector employed in conventional radioactivation analysis. In addition the heavy shielding necessitated by the high penetrating power of the high energy capture gamma rays introduces geometry factors which considerably reduce the total detection efficiency. The result is that if $\sigma'\theta' f' \geqslant \sigma\theta f$, thus, we have on the contrary $\epsilon' \leqslant \epsilon$.

Finally we have assumed that the thermal neutron flux used was the same in the application of the two methods. In fact whereas for conventional activation analysis the sample can be placed inside the reactor, where the thermal neutron flux can reach 10^{13} to 10^{14}n·cm^{-2}·sec^{-1}, the fact that the capture gamma-ray measurement must be performed during the irradiation necessarily means housing it outside, at the outlet of a channel in which the neutrons have been suitably filtered to eliminate fast neutrons and gamma rays from the reactor core. The thermal neutron flux obtainable under these conditions is of the order of 10^7 to 10^8n·cm^{-2}·sec^{-1} leading to a factor of 10^4 and 10^7 in favor of radioactivation analysis.

From the above considerations it transpires that, as things stand at present, analysis by capture gamma-ray detection is in general distinctly inferior to radioactivation analysis. Attempts at improvement should be directed towards an increase in ϵ', *i.e.* the detection volume, a maximum decrease in the sample-detector distance, and finally the development of channels delivering a high thermal neutron flux contaminated as little as possible by fast neutrons and gamma-ray radiation.

The elements most suitable for detection by capture gamma ray measurement can be foreseen. For different biological samples in fact it is possible to determine the elements giving the highest ratio $W\sigma'/A$. Table 1 shows the value of this ratio for 10 elements in blood, bone, hair and a typical plant sample (W is expressed in grams of the element per liter or per kg of sample and σ' in barns).

The order thus established may be slightly modified by the value for the different elements and by consideration of the number of capture photons

Table 1. Value of the ratio $W\sigma'/A$ for the principal elements of some typical biological samples.[a]

Blood		Bone		Hair		Plant tissue	
Element	$\frac{W\sigma'}{A}$	Element	$\frac{W\sigma'}{A}$	Element	$\frac{W\sigma'}{A}$	Element	$\frac{W\sigma'}{A}$
H	32.4	H	9	–	–	H	18.2
Cl	2.71	Cl	3.9	Cl	18.8	B	17.8
N	1.78	Ca	2.75	S	0.61	Cl	1.88
K	0.091	N	2.4	Fe	0.0061	N	1.6
Na	0.046	B	1.78	P	0.0049	K	0.76
B	0.046	P	0.72	Ca	0.0021	Ca	0.193
S	0.0325	Na	0.32			Na	0.027
Fe	0.022	K	0.08			S	0.016
P	0.0022	S	0.041			P	0.014
Ca	0.00067	Fe	0.0094			Fe	0.0066

[a] W is expressed in g/kg and σ' in barns.

per nuclear reaction (f') for the strongest line which is not very well known.

This table shows that the three elements H, N and B which cannot be measured by conventional neutron radioactivation are good subjects for capture gamma-ray determination. In addition, sulphur and phosphorus, at least in the case of bone and hair tissue, have an appreciable $W\sigma'/A$ ratio and we can hope to detect them in these biological media.

III. Material and Methods

A. THERMAL NEUTRON SOURCE

The neutrons used are obtained from a curved neutron guide built by the physicists of the Solid Physics group at the Saclay Center of Nuclear Studies [7]. It is made up of suitably shaped 2 cm-thick glass bricks, nickel-coated on the inner surface, forming a channel of rectangular internal cross section 2 cm × 5 cm resting on a long marble bracket. The radius of curvature of the channel leading from the reactor EL3 is 840 meters. The thermal neutrons are propagated in this guide by total reflection on the nickel walls and are dissociated from fast neutrons and fission gamma rays owing to the curvature of the channel. We thus obtain at the guide outlet a beam of thermal neutrons of wavelengths varying between 0.8 Å and a few tens of an Å, entirely free of fast neutrons and gamma-ray radiation.

Because of the effect of energy on the total reflection, the neutrons show a heterogeneous spatial distribution at the guide outlet. The maximum flux at this point is about $4.5 \times 10^7 n \cdot cm^{-2} \cdot sec^{-1}$ and the average flux slightly above $2 \times 10^7 n \cdot cm^{-2} \cdot sec^{-1}$.

B. PREPARATION OF SAMPLES

Whole blood was dried by freeze-drying. Bone samples were reduced to powder and oven-dried at 100 °C. Hair and plant matter (cabbage and brown Algae) were powdered and oven dried at 100 °C. A fraction of about 10 g of these various samples was dry ashed in a muffle furnace for 12 hours at 650 °C. The main purpose of this operation is to free the samples of hydrogen in order to obtain a capture spectrum for elements which would have their characteristic gamma rays masked by the Compton background of the 2.23 MeV hydrogen peak.

The samples thus prepared (0.2 to 3 g of dry powder and ash) were placed in cylindrical nuclear graphite containers of internal diameter 2 cm and depth 2 cm. Standards containing known quantities of the different elements investigated were also prepared in graphite containers.

During the irradiation the samples were arranged in the axis of the channel, 20 cm from its end, entirely surrounded except at the front by 5 mm-thick plates of sintered lithium-6 fluoride in order to prevent neutrons scattered by the sample from giving capture reactions with the surrounding materials. The irradiation time varied between a few minutes and 10 hours according to the samples.

In vivo irradiations were carried out on the antero-internal face of the tibia, in the diaphysic region of normal adult subjects. The leg, arranged vertically in the channel axis, was surrounded except for the neutron impact zone by plates of sintered lithium-6 fluoride. The irradiation time varied from 10 to 30 minutes.

C. SPECTROMETRIC MEASUREMENT DEVICE

This is made up of a coaxial lithium compensated germanium detector of 20 cm^3 active volume. The capacity of this detector is 48 pF including the connection to the transistorized field effect preamplifier. The resolution at the optimum voltage of 500 volts is 5.3 keV for the 1.33 MeV line of cobalt-60. A MAP 40 amplifier and a 4096 channel BM 96 memory unit with CA 13 digital to analogue converter (Intertechnique) analyses the impulses coming from the detector. The counting efficiency for the 1.33 MeV cobalt line is 6.5% that of a 3 in. × 3 in. sodium iodide crystal. The axis of the detector is arranged perpendicular to that of the neutron flux and facing the sample. The Ge(Li) crystal is surrounded by a 10 cm thick lead shield castle. A cylindrical opening of 4 cm diameter is provided in the axis of the detector. The front face of the lead shield castle is covered with 5 mm thick plates of sintered natural lithium fluoride. The detector-sample distance is 20 cm (Fig. 1).

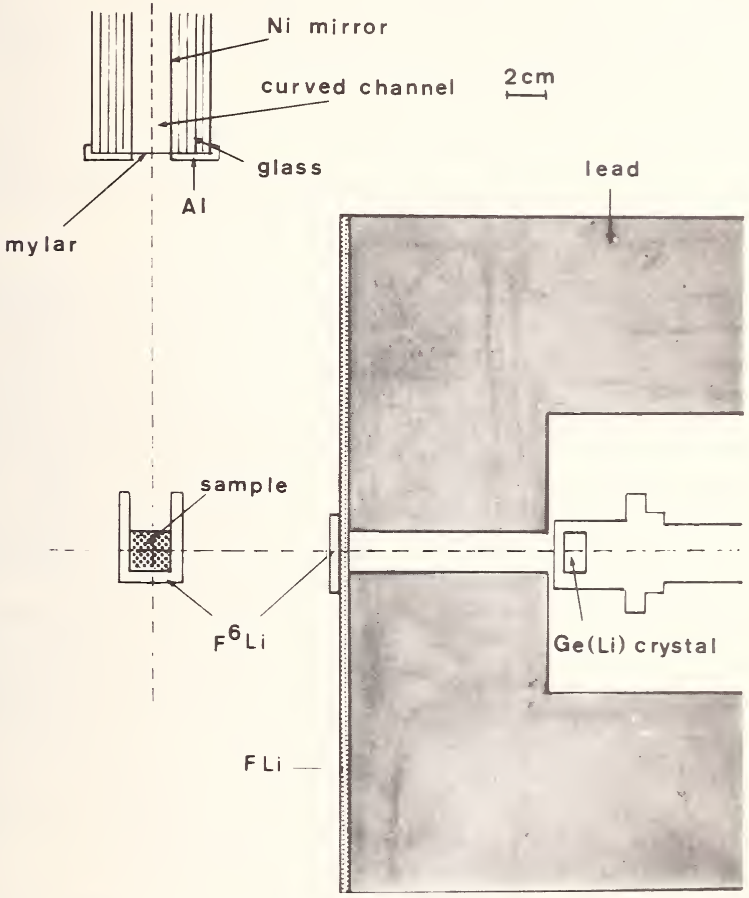

Figure 1. Diagram of the arrangement of the sample and detector with respect to the neutron source.

IV. Results and Discussion

A. ANALYSIS OF THE SPECTRA

Two types of recordings were made: the first in an energy band between 0 and 2 MeV, and the second between 0 and 8 MeV. Figure 2 shows the spectrum recorded over a period of 10 hours on a 25 ml sample of dried calcined blood. Most of the peaks observed were identified from work published by Greenwood *et al* [8] and Groshev *et al* [9]. The main

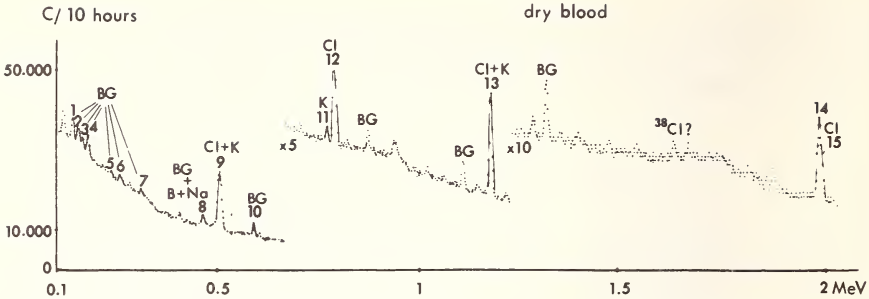

Figure 2. Capture gamma-ray spectrum between 0 and 2 MeV of a sample of calcined blood (sample volume: 25 ml, counting time: 10 hours).

elements detected in the sample are chlorine, probably sodium, potassium and boron. For each of these elements Table 2 shows the energy of the peaks opposite the numbers given on Figure 2. This table also shows the characteristic peaks of germanium, copper and nickel corresponding to the capture of neutrons, by the detector and its surroundings in spite of the shielding. Other peaks representing the background have not yet been identified. Sodium and boron cannot be differentiated since their characteristic peaks are identical (0.477 MeV). In the same way potassium can only be identified by the 0.777 MeV peak, its other lines (0.517 and 1.167 MeV) being common with those of chlorine.

The high energy spectrum recorded on the same blood sample, noncalcined, is shown in Figure 3. The lines observed are mainly double escape lines. To obtain the true energy levels, 1.02 MeV should be added to each of the following values. Here again the spectrum is dominated by the characteristic lines of chlorine (1 = 3.960 MeV, 3 = 4.490 MeV, 4 = 4.685 MeV, 5 = 5.085 MeV, 6 = 5.300 MeV, 7 = 5.590 MeV, 8 = 6.11 MeV, 9 = 6.38 MeV and 11 = 6.76 MeV). A nitrogen line can be perceived however (2 = 4.28 MeV), and also another at 4.51 MeV overlying the 4.490 MeV chlorine line.

Figure 4 shows the spectrum of a powdered bone sample recorded during an 8-hour irradiation. Only the high energy peaks are presented. The 4 elements detected are calcium, phosphorus, chlorine and nitrogen. Table 3 gives the characteristic energies of these elements. Another spectrum of calcined bone recorded in the 0 to 2 MeV energy range shows the same elements and also boron.

The spectrum obtained on hair (Fig. 5) after 8 hours counting (1 g of powdered hair) shows up the presence of nitrogen and sulphur (1 = 3.842 MeV, 2 = 4.392 MeV, 3 = 4.900 MeV).

In all the samples analyzed the 2.23 MeV hydrogen peak is predominant and is not shown on the figures in order to avoid overcrowding.

Table 2. Energy of the capture gamma rays of the spectrum of figure 3 (blood).

Chlorine	Peak number	9	12	13	14	15
	Energy (MeV)	0.518	0.792	1.168	1.949	1.957
Sodium	Peak number	8				
	Energy (MeV)	0.477				
Potassium	Peak number	9	11	13		
	Energy (MeV)	0.517	0.777	1.167		
Boron	Peak number	8				
	Energy (MeV)	0.477				
Germanium	Peak number	2	5	7	10	
	Energy (MeV)	0.173	0.253	0.327	0.595	
Copper	Peak number	1	3	4		
	Energy (MeV)	0.161	0.186	0.197		
Nickel	Peak number	1	6	8		
	Energy (MeV)	0.161	0.273	0.473		

On referring to Table 1 it is observed that apart from chlorine, which was not detected in the hair sample, the elements shown up in the blood and bone samples are those with the highest $W\sigma'/A$ ratio.

B. Quantitative Measurements

The mass of an element cannot be measured from its capture gamma-ray spectrum by simple comparison with a standard subjected to the same neutron flux.

Because of the high concentration of hydrogen in biological media it is practically impossible to obtain a homogeneous irradiation with a

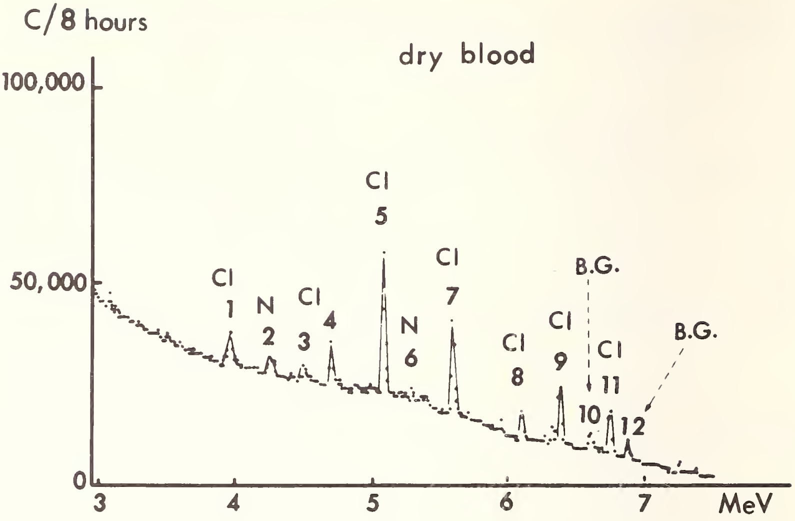

Figure 3. Capture gamma-ray spectrum between 3 and 8 MeV of a sample of dried blood (weight of sample : 4.49 g, counting time: 8 hours).

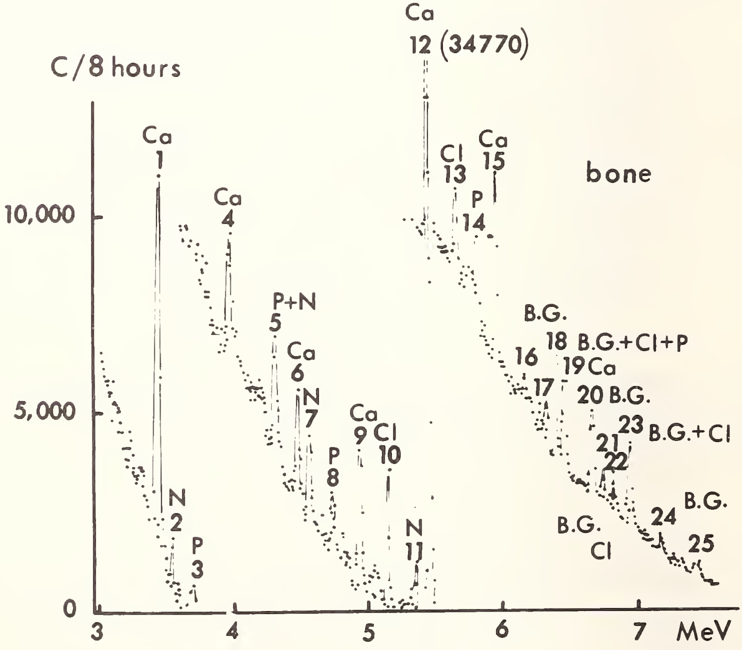

Figure 4. Capture gamma-ray spectrum between 3 and 8 MeV of a sample of bone (weight of sample: 8 g, counting time : 8 hours).

Table 3. Energy of the capture gamma rays of the spectrum of figure 5 (bone).

Calcium								
Peak number	1	4	6	9	12	15	19	
Energy (MeV)	3.397	3.924	4.418	4.870	5.393	5.903	6.415	
Chlorine								
Peak number	10	13	18	22	23			
Energy (MeV)	5.085	5.591	6.390	6.768	6.893			
Phosphorus								
Peak number	3	5	8	14	18			
Energy (MeV)	3.645	4.240	4.660	5.760	6.390			
Nitrogen								
Peak number	2	5	7	11				
Energy (MeV)	3.490	4.249	4.510	5.298				
Background								
Peak number	16	17	18	20	21	23	24	25
Energy (MeV)	6.228	6.288	6.390	6.61	6.700	6.893	7.13	7.42

directional flux of thermal neutrons. Studies performed on a phantom simulating the tissues, inside which gold leaves were distributed at different depths, have shown that the thermal neutron flux is attenuated by a factor of two per cm of tissue [10]. Comparison of the radioactivity of the sample with that of a standard as practiced in conventional radioactivation analysis would only be possible if the elementary composition, at least as far as the main elements are concerned, and the geometry of the standard were absolutely identical with those of the sample. In practice these conditions are more or less impossible to fulfill.

The internal standard method, as proposed by Isenhour and Morrison for the determination of boron in boric acid [3] and by Lenihan *et al* for the determination of intrathyroid iodine by radioactivation *in vivo* [11], can be used to make quantitative measurements in the case of capture

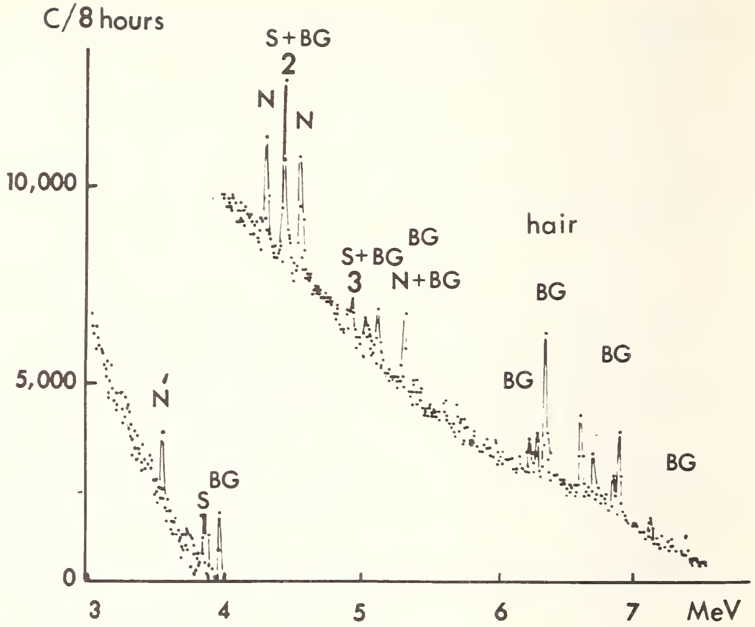

Figure 5. Capture gamma-ray spectrum between 3 and 8 MeV of a sample of hair (weight of sample : 1 g, counting time: 8 hours).

gamma-ray analysis. We applied this method to the determination of boron, chlorine and hydrogen in two different plant tissues: a powdered cabbage (*Brassica oleracea*) of well-known elementary composition [12], and a brown Algae (*Fucus vesiculosus*). The internal standard was mercury mixed in known quantity, in the form of red oxide, with powdered and dried plant sample. The standard was obtained by mixing known amounts of glucose, red oxide of mercury, sodium chloride and boric oxide.

Figure 6 shows the spectrum obtained during a 10 minute irradiation of a sample of powdered fucus (1.84 g powder and 0.0188 g HgO). From left to right can be seen the peaks at 0.370 MeV (Hg, 1), 0.477 MeV (boron, 2), 0.511 MeV (chlorine and hydrogen, 3), 0.788 MeV (chlorine, 4), 1.165 MeV (chlorine, 5), 1.201 (hydrogen, 6) and 2.23 MeV (hydrogen, 7).

On Table 4 are given the masses of these different elements calculated from capture gamma-ray spectra such as that of Figure 6 and that of the standard. We find from these determinations that the results, so far as pulverized cabbage is concerned, agree with those obtained on the same sample by other methods [12]. The results obtained on powdered fucus are compared with the published data [13]. The detection sensitivity of

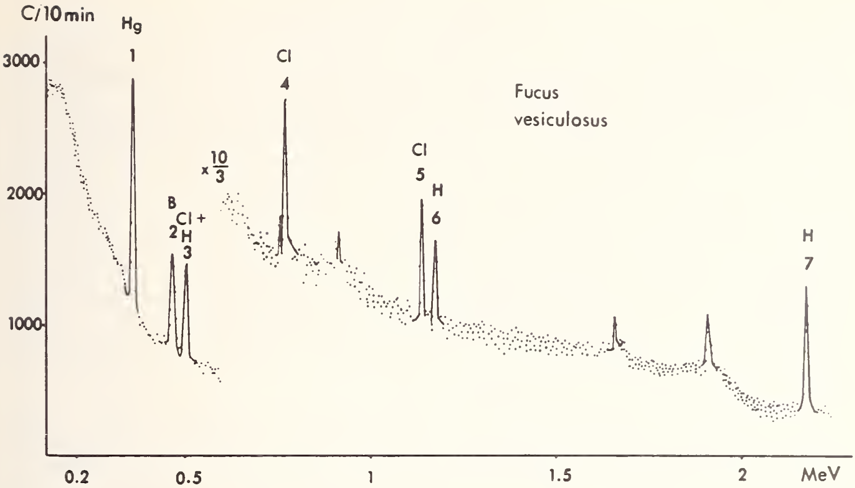

Figure 6. Capture gamma-ray spectrum of a powdered *fucus vesiculosus* sample (weight of sample: 1.84 g, counting time: 10 minutes).

the method described can be estimated at one µg for boron, one mg for chlorine and about 10 to 20 mg for hydrogen.

The results show clearly the effectiveness of using an internal standard. However, in the experiment described, the sample was contaminated with the mercury added which made it difficult to use for other measurements. To avoid this drawback it would probably be easy to take a natural component of the sample (chlorine for example) as an internal standard, its concentration being determined by another method (conventional radioactivation for example).

Table 4. Boron, hydrogen and chlorine concentrations of two plant samples (*Fucus vesiculosus and Brassica oleracea).*

Sample	Element	Results	Results taken from the literature (µg/g)		
	Boron	164	120		[13]
Fucus vesiculosus	Hydrogen	42,000	41,000		[13]
	Chlorine	28,000	4,700		[13]
	Boron	52.3	50.9	± 4.7	[12]
Brassica oleracea	Hydrogen	82,000	55,000		[13]
	Chlorine	3,020	3,330	± 1,060	[12]

C. MEASUREMENTS *in vivo*

During localized neutron irradiation of the tibia in normal subjects it was possible to measure the sodium, calcium and chlorine mass ratios by radioactivation [14]. However, since some of the sodium and all the chlorine are exchangeable in this tissue, a fraction of these elements leaves the irradiated zone during neutron bombardment with a biological half life of the same order of magnitude as the irradiation time. Thus to determine the amount of sodium and chlorine present in the bone, by activation *in vivo,* a correction allowing for these biological half lives must be applied to the gamma-ray spectrometry measurements of the radioelements formed. The fraction of exchangeable calcium in the bone is too small to be detected by activation.

The emission of capture gamma rays on the other hand is independent of both the physical and the biological half lives, which means that the area of the capture peaks recorded during irradiation is directly proportional to the mass of the elements irradiated whatever their rate of renewal.

The spectrum of Figure 7 was recorded over a period of 10 minutes during an experiment of this kind. From left to right the 5.090 MeV chlorine, the 5.393 MeV calcium and the 5.598 MeV chlorine peaks can be seen.

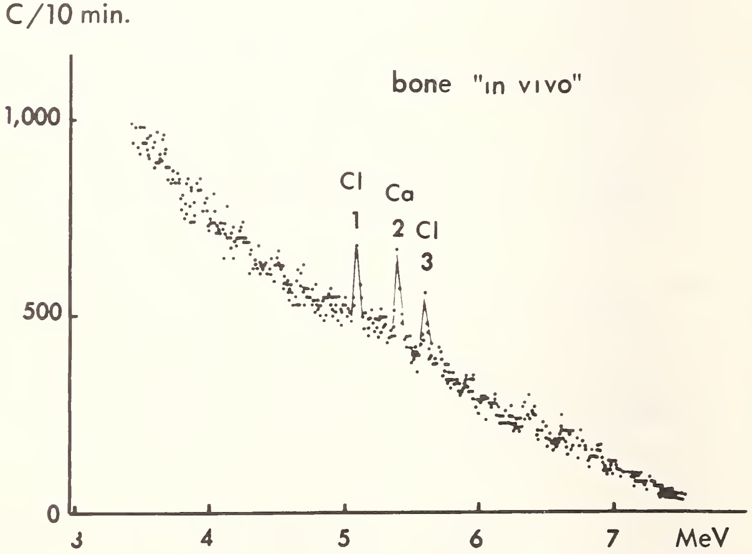

Figure 7. Capture gamma-ray spectrum of a human tibia obtained *in vivo* (counting time: 10 minutes).

It was possible to calculate the Ca/Cl ratio from these three peaks. The result was identical with that found from the spectra recorded during the decay of calcium-49 and chlorine-38 after irradiation. We were thus able to verify, that the estimation of the biological half life of chlorine in bone by the study of these spectra was correct.

V. References

[1] Foglio Para, A., and Mandelli Bettoni, M., Energia Nucleare **11**, 11, 612-615 (1964).

[2] Lussie, W. G., and Brownlee, J. L., in Proceedings of the 1965 International Conference on "Modern Trends in Activation Analysis", Texas A & M Univ., 1965, pp. 194-199.

[3] Isenhour, T. L., and Morison, G. H., Anal. Chem. **38**, 162-167 and 167-169 (1966).

[4] Lombard, S. M., Isenhour, T. L., Heints, P. H., Woodruff, G. L., and Wilson, W. E., Int. J. Applied Rad. and Isotopes **19**, 15-22 (1968).

[5] Vartapetyan, B. B., Dmitrovskii, A. A., Alkhazov, D. G., Lemberg, I. Kh., Girshin, A. B., Gusinskii, G. M., Starikova, N. R., Erofeeva, N. N., and Bogdanova, I. P., Biochemistry **31**, 759 (1966).

[6] Rundo, J., and Bunce, L. J., Nature (G.B.) **210**, No. 5040, 1023-1024 (1966).

[7] Farnoux, B., Hennion, B., and Fagot, J., Conference on the Inelastic Scattering of Neutrons, Copenhagen 20-25/5/68, I.A.E.A., Vienna.

[8] Greenwood, R. C., and Reed, J. H., "Prompt Gamma Rays from Radiative Capture of Thermal Neutrons", I.I.T. Research Institute, Chicago. Oct. 14, 1965, distributed by Clearinghouse, Department of Commerce, Washington, D.C.

[9] Groshev, L. V., Demidov, A. M., Lutsenko, V. N., and Pelekhov, V. I., Atlas of Gamma Ray Spectra from Radiative Capture of Thermal Neutrons, Pergamon Press, 1961.

[10] To be published.

[11] Lenihan, J. M. A., Comar, D., Riviere, R., and Kellershohn, C., Nature (G.B.) **214**, No. 5094, 1221 (1967).

[12] Bowen, H. J. M., The Analyst **92**, 124-131 (1967).

[13] Bowen, H. J. M., in Trace Elements in Biochemistry, Academic Press, 1966.

[14] Comar, D., Riviere, R., Raynaud, C., and Kellershohn, C., in Radioisotope in Clinic and Research, Vol. VIII, Urban & Schwarzengerg, Munich (in press).

ELEMENT IMBALANCES OF ATHEROSCLEROTIC AORTAS[1]

W. H. Strain, C. G. Rob, and W. J. Pories

University of Rochester, Rochester, New York

R. C. Childers, M. F. Thompson, Jr., and J. A. Hennessen

Wright-Patterson AFB, Ohio

F. M. Graber

Gulf General Atomic, San Diego, California

I. Introduction

Activation analysis has been used to determine element imbalances that may contribute to the development of atherosclerosis. The analyses were conducted on normal and atherosclerotic aortas from rats and man as well as on a human abdominal aortic aneurysm. The procedure was restricted to the determination of Ca, Cd, Co, Cu, Mg, Mn, Se, V, and Zn, since these elements seem to be most important to arterial metabolism. It has been established that aortic calcium is greatly elevated in atherosclerosis [1,2], but there is little data on the changes in content of the other elements in arterial tissue. The investigation was carried out to provide additional information on vascular trauma and degeneration. It is an extension of our work on oral zinc therapy for the treatment of atherosclerosis [3,4].

II. Experimental

A. Apparatus and Reagents

The activation analysis procedure comprised several precipitations and novel extraction operations for the radiochemical separations. The samples were irradiated in the TRIGA Mark I reactor at a thermal-neutron flux of $1.8 \times 10^{12} n \cdot cm^{-2} \cdot sec^{-1}$. The radiochemical separations were carried out by precipitating insoluble phosphates and sulfates, and by extracting soluble complexes of diethyldithiocarbamic acid in ethyl acetate at various pH levels.

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B. PROCEDURE

Aortas from rats and man were collected for the analyses. Wexler [5] has shown that old female breeder rats show atherosclerosis due to calcium and other deposits, but that young virgin females are free of these changes. Accordingly, whole aortas from freshly killed young virgin and old breeder female rats were collected. It was found, and verified histologically, that these rat aortas could be graded by weighing into the following degrees of atherosclerosis: none ($<$100 mg); slight (135-150 mg); moderate (150-165 mg); and severe ($>$185 mg).

For the human aortic tissue, material was collected from the autopsy of a 70 year old male and from the operative removal of an aortic aneurysm in a 60 year old man. The aortic tissue from the 70 year old male was divided into media:intima sections showing slight, moderate, and severe atherosclerosis, since calcification is always greater in the media [1]. The aneurysm was divided into five sections as follows: (1) a thrombus at the site of the major breakdown of the arterial wall; (2) a media section with severe atherosclerosis; (3) a media section with slight atherosclerosis; (4) an adventitia section with slight atherosclerosis; and (5) and adventitia layer with severe atherosclerosis. The degree of atherosclerosis was established histologically for each section.

Preparation for analysis of the aorta tissue from rats and man was essentially the same. After dissection from the rats, the aortas were placed on ash-free filter paper and the extraneous outer tissue stripped off by means of a Bard-Parker blade. This procedure also expelled any blood that may have been retained in the arterial segment. The human aortas were similarly stripped free of extraneous outer tissue and then cut with the aortas supported on plastic sheeting. The cleaned tissues were then cut into small pieces with quartz knives, dried at 110 °C, and ground to a powder in quartz apparatus. Weighed aliquots of each sample were placed in Polyvials. Prior to use, these vials had been cleaned with nitric acid, washed with deionized water, and dried with ethyl alcohol.

Vialed tissue and comparator standards of Ca, Cd, Co, Cu, Mg, Mn, Se, V, and Zn were irradiated for 30 minutes in the TRIGA Mark I nuclear reactor at a thermal-neutron flux of $1.8 \times 10^{12} \mathrm{n \cdot cm^{-2} \cdot sec^{-1}}$. After irradiation, the samples were rapidly transferred to Erlenmeyer flasks and were quickly dissolved in the presence of evaporated carriers of Mn, Cu, Zn, V, Mg, Se, Cd, and Co (24 mg, 2 mg, 6 mg, 0.13 mg, 26 mg, 0.4 mg, 1 mg, and 0.4 mg, respectively). Hot 95% H_2SO_4 and 90% HNO_3 were used to dissolve the samples. After the samples were dissolved, 102 mg of the Ca carrier was added and the suspension centrifuged. The precipitate of $CaSO_4$, *etc.,* was saved and the supernatant was made basic with NH_4OH to pH 9. Ten ml of a 4% aqueous solution of sodium diethyldithiocarbamate were added to form the diethyldithiocarbamates of Mn, Cu, Zn, Cd, and Co. Thirty ml of ethyl acetate were added and the mixture shaken so that the Mn, Cu, Zn, Cd, and Co complexes extracted into the organic phase. After separating the organic layer, the aqueous phase was adjusted to pH 5 with nitric and acetic acids, and additional sodium diethyldithiocarbamate solution added to form the diethyldithiocarbamates of V and Se. The complexes of V and Se were extracted with ethyl acetate and the organic solution placed in a Polyvial and counted for ^{52}V and ^{81m}Se. The half life values and radiation energy in MeV for the radionuclides of the radiochemical separation are collected in Table 1.

The aqueous phase from the V and Se extractions was combined with $CaSO_4$ precipitate. After redissolving any $CaSO_4$ with acid the resulting solution was used to precipitate the phosphates of Ca and Mg in a basic solution by the addition of dilute $(NH_4)_2HPO_4$. The ammonium phosphate precipitate of Ca and Mg was redissolved and reprecipitated, and finally washed with water and dissolved with HNO_3. This nitric acid solution of Ca and Mg was placed in a Polyvial and counted for ^{49}Ca and ^{27}Mg.

Table 1. Half life and radiation energy of radionuclides measured in neutron activation analysis of calcium, cadmium, cobalt, copper, magnesium, manganese, selenium, vanadium, and zinc in aorta tissue.

Radionuclide	Half life	Radiation energy in MeV
^{49}Ca	8.8 min	3.1
^{111m}Cd	49 min	0.24
^{60}Co	5.24 y	1.17
^{60m}Co	10.5 min	0.059
^{64}Cu	12.8 h	0.51
^{27}Mg	9.5 min	0.84
^{56}Mn	2.58 h	0.84
^{75}Se	120 d	0.402
^{77m}Se	17 sec	0.160
^{81m}Se	57 min	0.103
^{52}V	3.76 min	1.44
^{69m}Zn	13.8 h	0.438

The organic phase containing the diethyldithiocarbamate complexes of Mn, Cu, Zn, Cd, and Co was washed three times with water and back extracted with 0.16 *M* HNO_3 to remove Mn and Zn. The ethyl acetate phase was concentrated and placed in a Polyvial for counting of ^{60m}Co, ^{111m}Cd, and ^{64}Cu. The 0.16 *M* HNO_3 phase containing the ^{56}Mn and ^{69m}Zn was concentrated and placed into a Polyvial for counting of these two radionuclides. After decay of approximately a week, the V and Se fraction was counted for the long-lived ^{60}Co.

The radiochemical yields of Mn, Cu, Zn, Cd, Co, Ca, Mg, Se, and V were obtained by reirradiation (comparing with standards) for 12 seconds using the pneumatic tube of the TRIGA Mark I nuclear reactor at a thermal-neutron flux of $4.3 \times 10^{12} n \cdot cm^{-2} \cdot sec^{-1}$. The radionuclides used for yield indicators were those shown in Table 1 with the exception of ^{60}Co and ^{75}Se. In the manganese-zinc fraction ^{56}Mn is immediately observable following the activation and can be measured soon. It is best to allow the sample to decay overnight prior to measuring the ^{69m}Zn yield indicator. All the pulse-height spectral digital data were placed on IBM cards and processed with a computer program to provide the values in parts per million (ppm). The calculations were made with a Univac 1108 computer.

III. Results and Discussion

A. Results

The analytical results given in Tables 2 and 3 show that there are significant differences in element content between normal and atherosclerotic tissue. As the degree of atherosclerosis increased, the element content in ppm changed as follows: Ca from <350 to 170,000; Cd from undetectable to 1.4; Co from undetectable to 0.34; Mg from <110 to 880; Mn from 0.081 to 1.9; Se from <0.4 to 0.6; Zn from 30 to 152. The changes in Cu were inconsistent, with the low value of 1.73 probably significant but the high 10 ppm due to vial contamination. V could not be detected.

B. Discussion

The data appear to support the use of zinc therapy in the treatment of atherosclerotic occlusive disease. Ca:Zn ratios have been calculated for Tables 2 and 3, and are added as a final column. In all the atherosclerotic tissues there is a very unfavorable Ca:Zn ratio. Since normal calcium metabolism seems dependent on adequate zinc [6], there are indications that the human diet may be inadequate in available zinc if atherosclerosis develops.

Table 2. Element content by activation analysis of aortas with varying degrees of atherosclerosis.[a]

Element content

Rat[b]

Degree of atherosclerosis	Ca	Cd	Co	Cu	Mg
None	<350	<0.13	<0.30	3.86 ± 0.07	<110
Slight	6,970 ± 380	<0.15	<0.14	3.29 ± 0.05	880 ± 49
Moderate	27,000 ± 1,000	<0.49	0.19 ± 0.09	4.35 ± 0.09	570 ± 60
Severe	36,000 ± 2,000	<0.32	0.34 ± 0.08	3.46 ± 0.09	615 ± 56

	Mn	Se	V	Zn	Ca:Zn
None	0.99 ± 0.05	<0.8	<0.13	77 ± 5	<5
Slight	0.78 ± 0.01	<0.9	<0.058	106 ± 6	66
Moderate	0.74 ± 0.01	<0.4	<0.21	136 ± 4	198
Severe	1.26 ± 0.01	<0.6	<0.044	152 ± 4	237

Man[c]

	Ca	Cd	Co	Cu	Mg
Slight	1,800 ± 770	<1.1	0.10 ± 0.1	10.2 ± 0.2	210 ± 48
Moderate	2,560 ± 407	<0.33	<0.11	5.7 ± 0.3	<395
Severe	8,950 ± 375	<0.28	<0.1	4.3 ± 0.2	475 ± 15

	Mn	Se	V	Zn	Ca:Zn
Slight	0.34 ± 0.2	<1.0	<0.14	37 ± 3	49
Moderate	0.94 ± 0.04	<1.0	<0.13	37 ± 5	69
Severe	0.23 ± 0.01	0.6 ± 0.1	<0.14	48 ± 4	186

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[a] Results in parts per million.

[b] Aortas from six rats for each category.

[c] Intima : media sections from the aorta were used.

The other elements appear to be implicated in the development of atherosclerosis in varying degrees. The low level of Cd is consistent with the absence of heavy industry in the Rochester area. The low content of copper in one of the tissue sections from the aneurysm is in accord with the development of similar lesions in poultry [7] and swine [8] on copper deficient diets. The levels of Mg, Mn, Se, and V must be studied further to discover evidence of deficiency of sufficiency of these elements in Monroe County, or Western New York State.

Table 3. Element content by activation analysis of human abdominal aneurysm.[a]

Section of aneurysm[a]	Element content									
	Ca	Cd	Co	Cu	Mg	Mn	Se	V	Zn	Ca:Zn
Thrombus	520 ± 150	<0.20	<0.04	3.33 ± 0.06	1070 ± 109	0.081 ± 0.004	<11	<0.042	34.8 ± 0.9	15
Media (severe)	170000 ± 9000	<1.1	<0.21	1.73 ± 0.09	1960 ± 180	0.17 ± 0.01	< 0.42	<0.11	143 ± 3	1188
Media (slight)	3460 ± 310	1.4 ± 0.2	<0.08	4.5 ± 0.2	286 ± 21	1.9 ± 0.1	< 1.3	<0.37	63 ± 5	55
Adventitia (slight)	530 ± 150	<0.22	<0.12	2.08 ± 0.05	308 ± 22	0.88 ± 0.01	0.2 ± 0.18	<0.053	30 ± 3	18
Adventitia (severe)	2970 ± 460	<0.23	<0.13	4.00 ± 0.09	360 ± 33	0.63 ± 0.03	<0.7	<0.10	35.2	85

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[a] Results in parts per million.

[b] Degree of atherosclerosis given in parenthesis.

IV. References

[1] Giertsen, J. Chr., Atherosclerosis in an Autopsy Series, Supplement 170 (1964) to Acta. Pathol. Microbiol. Scand. p. 142.

[2] Yu, S. Y., in Cowdry's Atherosclerosis, H. T. Blumenthal, Ed., Charles C. Thomas, Springfield, Illinois, 1967, pp. 170-192.

[3] Pories, W. J., Rob, C. G., Smith, J. L., Henzel, J. H., and Strain, W. H., Proc. 7th Intern. Congress. Gerontol. (Vienna), 1966, p. 449.

[4] Plecha, F. R., Strain, W. H., Rob, C. G., and Pories, W. J., J. Soc. Air Force Clin. Surg., in press.

[5] Wexler, B. C., J. Atherosclerosis Res. **4**, 57 (1964).

[6] Luecke, R. W., in Zinc Metabolism, A. S. Prasad, Ed., Charles C. Thomas, Springfield, 1966, pp. 202-214.

[7] O'Dell, B. L., Hardwick, B. C., Reynolds, G., and Savage, J. E., Proc. Soc. Exp. Biol. Med. **108**, 402 (1961).

[8] Coulson, W. F., and Carnes, W. H., Am. J. Path. **43**, 945 (1963).

A USEFUL NEUTRON ACTIVATION ANALYSIS METHOD FOR THE DETERMINATION OF TELLURIUM IN HUMAN TISSUES

A. Abu-Samra and G. W. Leddicotte

Research Reactor Facility
University of Missouri
Columbia, Missouri

I. Introduction

The role of trace tellurium in human physiological processes is not fully understood and health-related researchers are beginning to seek analytical methodology that can be used to produce data so that the functions of less known species, such as tellurium, may be described. In the interests of providing a usable methodology, a neutron activation method has been developed to determine tellurium in human tissues in concentrations of parts per million or less. The developed methodology permits rapid and routine assays of these types of biological materials. The method is easily adapted to other sample materials.

II. Experimental

Although the element, tellurium, contains several stable isotopes (see Table 1) that can be made radioactive by thermal neutron bombardment, the nuclear reaction, $^{130}\mathrm{Te}(n,\gamma)$ $^{131}\mathrm{Te} \xrightarrow{\beta-} {}^{131}\mathrm{I}$, were used to complete the analyses performed in this investigation. A destructive distillation of the irradiated sample was used to free the ^{131}I (8.05d) and the I^- carrier from interferences of ^{24}Na, ^{42}K, ^{64}Cu and ^{56}Mn, and other radioactive species produced in the sample during the activation. The ^{131}I and its carrier were removed from the distillate by solvent extraction with chloroform and then precipitated as AgI to determine the chemical yield of the experiment.

A. SAMPLE PREPARATION

0.1 to 0.2 gram portions of dried tissues were placed in a quartz ampule and sealed. Comparator samples containing 10-15 mg of tellurium oxide were also placed in similar quartz ampules. Samples and standards were placed inside an aluminum capsule which was sealed and irradiated inside the reactor.

Table 1. Tellurium isotopes produced by irradiation with neutrons [1, 2].

Target nuclide	Relative percentage abundance	Cross section (barn)	Product nuclide	Half life	Gamma-ray energy, (MeV)
^{120}Te	0.089	2.0	^{121m}Te	154 d	0.21
		0.3	^{121}Te	17 d	0.57
^{122}Te	2.46	1.1	^{123m}Te	121 d	0.159
^{124}Te	4.61	5	^{125m}Te	58 d	0.11
^{126}Te	18.71	0.9	^{127}Te	9.5 h	0.42
^{128}Te	31.79	0.14	^{129}Te	70 min	0.45
^{130}Te	34.49	0.2	^{131}Te	25 min	0.15, 0.45

B. APPARATUS

The distillation apparatus consisted of a 100-ml Erlenmeyer flask equipped with a distillate arm composed of a condenser tube and auxillary glass fittings. The flask was also fitted with a glass tube that reached to the bottom so that an air current could be applied to the flask and reagents added during the distillation. The distillate was collected in a 50-ml Erlenmeyer flask that contained 25 ml of 1 *N* NaOH and 5 ml of 100-mg/ml $NaHSO_3$.

The ^{131}I recovered was measured by a radiation detection and measurement system composed of a 3 in. × 3 in. NaI(Tl) scintillation crystal connected to a Nuclear-Chicago Model 24-2, 400-channel gamma-ray spectrometer.

Sample irradiations were carried out in the University of Missouri's research reactor. At the time the irradiations were made, the reactor was operating at a power level of 5 MW. The irradiation facility used for this work has a thermal neutron flux of $3 \times 10^{13} n \cdot cm^{-2} \cdot sec^{-1}$ at this power level.

C. REAGENTS

Reagent grade KI, HNO_3, H_2SO_4, H_2SO_3, $KMnO_4$, H_2O_2, $CHCl_3$, NaOH, $NaHSO_3$, and $AgNO_3$ were used as the reagents in the radiochemical separation procedure. Purified TeO_2 was used to prepare the tellurium comparator samples.

D. PROCEDURE

Each of the hard and soft tissues and the tellurium comparator samples were irradiated for 24-30 hours (at a thermal neutron flux of $3 \times 10^{13} \mathrm{n \cdot cm^{-2} \cdot sec^{-1}}$). After irradiation the samples were held in storage area for at least 5 hours in order that the induced ^{131}Te could decay into ^{131}I. After this decay period, the sealed quartz ampule containing the irradiated tissue was opened, and its content was transferred into a porcelain crucible. To that crucible 200 mg of KI and two grams of a mixture of 53% KNO_3 and 47% $NaNO_3$ were added. The crucible was covered and heated for five minutes on the flame in order to ash the organic tissue. After the ignition and ashing process, the crucible was cooled and its content was dissolved in 10 ml of H_2O then transferred into the Erlenmeyer flask. Into that flask 3 ml of 1 *M* $NaNO_2$ was added and the flask was connected to the distillation apparatus and air flow system. The air flow into the flask was controlled at a rate of 0.5 cm^3/sec. After this operation 5 ml of 18 *M* H_2SO_4 were added to the flask through the side and I_2 was liberated. The temperature of the mixture was raised ten minutes later to near boiling by using an electric hot plate which caused ^{131}I and I_2 to distill from the mixture.

The collected distillate was then transferred to a 100-ml separatory funnel to which $NaNO_2$, 50% v/v HNO_3 and 10 ml of $CHCl_3$ had been added. The mixture was shaken to extract the free iodine into the chloroform layer. The $CHCl_3$ was transferred to a second 100-ml separatory funnel and washed with 10 ml of H_2O. The $CHCl_3$ layer was then transferred to a beaker containing 10 ml of $AgNO_3$ (50 mg/ml) and stirred by a magnetic stirrer. The ^{131}I and I carrier precipitated as AgI. This precipitate was filtered and washed with water and acetone. After it was dried it was weighed and counted.

To complete the analysis, the 0.362 gamma ray from ^{131}I was measured and its intensity was compared to the ^{131}I produced in the tellurium comparator that had been irradiated and counted under the same conditions.

III. Results and Discussion

After correcting for chemical yield and taking the ratio of the counts of ^{131}I from both the sample and the standard, the concentration of the tellurium in the tissue was obtained. The data given in Table 2 are typical of these analyses and show the probable concentration of tellurium in human hard and soft tissues.

This study, in addition to providing a rapid method (about 1 hour of radiochemical processing) for the determination of tellurium in animal and human tissues, involved an investigation of the degree of exchange

Table 2. Neutron activation analysis determination of tellurium in human tissues.

Tissue	Tellurium concentration in dry tissue (ppb)	
	Assay #1	Assay #2
Spleen	48	16
Muscle	24	10
Liver	N.D.	14
Blood	39	35
Lung	120	82
Brain	N.D.	22
Testis	49	65
Ovaries	350	220
Kidneys	45	90
Bone	39	37
	62	28

between the ^{131}I in the irradiated sample and the iodine carrier. Complete exchange between these species was observed. Further work has been carried out to achieve increased sensitivity of the method. Refinement of methodology concerned with speed of analysis, sample preparation prior to analysis, irradiation of sample, and radiochemical processing, continues to be studied as more samples are being analyzed. Each of these parameters will be discussed in detail.

The significance of this investigation is such that it provides a specific and sensitive method for the determination of trace tellurium in biological materials. Its worth to health-related research concerned with an understanding of the role of trace tellurium in body metabolic processes will be increased as additional samples are analyzed.

IV. References

[1] Lederer, Hollander, and Perlman, Table of Isotopes, John Wiley & Sons, Inc., New York 1968.

[2] Goldman, David, The Chart of Nuclides, General Electric Company, Schenectady, New York 1966.

NEUTRON ACTIVATION ANALYSIS OF BRAIN FOR COPPER AND MANGANESE[1]

Edward D. Bird

Bowman Gray Medical School
Winston-Salem, North Carolina

J. F. Emery, S. B. Lupica, and W. S. Lyon

Analytical Chemistry Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee

I. Introduction

In previous studies investigating the effect of a tranquilizing drug phenothiazine on the concentration of manganese in the basal ganglia of the sub-human primate brain it was found that there was a significant increase in manganese and that this increase appeared to be associated with an increased amount of pigment in the brain. Since this area of the brain has the propensity to concentrate a number of cations it was considered important to measure other metals in the basal ganglia of primates after phenothiazine.

Copper as well as manganese is concentrated in biological pigmented tissues, and the clinical effects of this metal on the brain are similar to manganese. It was decided therefore to measure copper in addition to manganese in the various nuclei of the brain of our phenothiazine treated primates.

The amount of tissue available for analysis is quite small, and neutron activation analysis was therefore chosen as the method for measurement of these cations. The high concentrations and good neutron cross section of sodium and chloride results in the production of 15 h ^{24}Na and 37 min ^{38}Cl. The gamma-ray spectra of these nuclides obscure the peaks for copper and manganese. A recent radiochemical separation utilizing antimony pentoxide to remove sodium from activated samples has been described by Girardi [1]. We used such a technique in our procedure and were able to measure both copper and manganese in our samples simultaneously.

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II. Experimental

Animals were treated with phenothiazine for variable time periods and then sacrificed. Tissues were dissected free using plastic instruments, dried in a vacuum oven in nonmetallic containers, and then transferred to plastic vials for neutron activation analysis in the Oak Ridge National Laboratory Research Reactor (ORR). Samples were irradiated for 2 minutes at a neutron flux of $1.5 \times 10^{13} n \cdot cm^{-2} \cdot sec^{-1}$. The tissue sample plus 0.1 mg each of Cu and Mn carrier was then digested with fuming HNO_3 containing a few drops of H_2SO_4, and the mixture heated to remove chlorine. After further nitric acid digestion the samples were cooled and passed through a 0.5 gram column of Sb_2O_5 that had been preconditioned with 9 *N* HNO_3. The eluate was counted on a 3 in. × 3 in. NaI crystal using a 512 multichannel analyzer.

Typical gamma-ray spectra taken before (Figure 1) and after (Figure 2) the Sb_2O_5 separation are shown.

Total volume of sample plus 9 *N* HNO_3 washes passed through the Sb_2O_5 column was seven ml. The eluates were collected and counted on a 3 in. × 3 in. NaI(Tl) detector equipped with a 512 channel analyzer. For ^{64}Cu the 0.51 MeV gamma ray photopeak was integrated, while for ^{56}Mn the 0.84 MeV gamma ray photopeak was used. After appropriate corrections for decay, the photopeak areas of the samples were compared with those of the standards, and the amount of Cu and Mn present determined by the usual calculation. Quantitative recovery of both Cu and Mn activity was determined by passing known amounts of ^{64}Cu and ^{56}Mn through the system in simulated experiments. Quantitative recovery was noted in a total passed through volume of 6 ml.

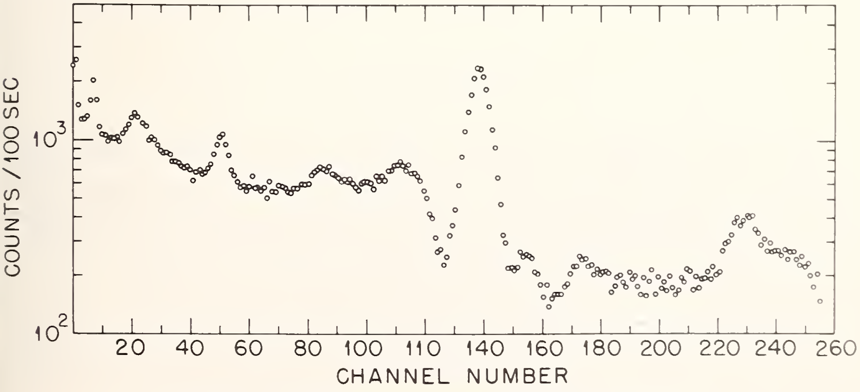

Figure 1. Tissue before separation (~10 keV/channel).

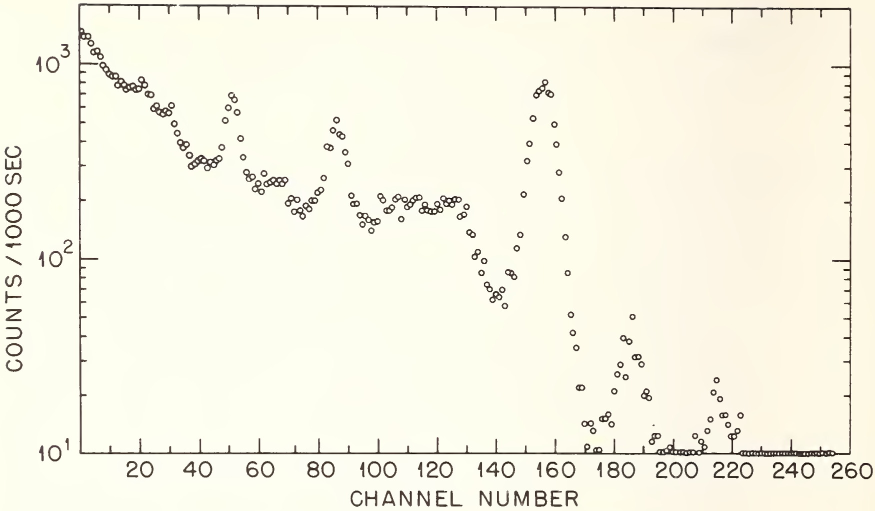

Figure 2. Tissue after separation (~10 keV/channel).

Table 1. Copper and manganese in brain tissue.

Tissue	Number of samples	Treated Copper[a] (μg/g)	Treated Manganese[a] (μg/g)	Controls Manganese[a] (μg/g)
Putamen	9	32.4 ± 5.4	2.05 ± 0.24	1.88 ± 0.31
Caudate	7	32.7 ± 3.7	2.05 ± 0.19	1.81 ± 0.08
Globus Pallidus	8	25.2 ± 7.5	2.05 ± 0.28	2.09 ± 0.23

[a] Dry weight basis.

III. Results

Each tissue sample was done in duplicate. The average copper and maganese concentrations in the various nuclei of the basal ganglia from treated animals appears in Table 1. The average manganese concentration in basal ganglia of control animals is listed in Table 1 for comparison. We have not measured the copper concentration in control animals.

Although there is a significant increase in the manganese concentration of the basal ganglia in animals treated for one month, the present results indicate that there is no significant difference in manganese concentration when animals are treated for longer periods up to one year.

The use of the Sb_2O_5 technique provides a rapid and clean method for removal of sodium for the simultaneous measurement of copper and manganese.

IV. Reference

[1] Girardi, F., and Sabbioni, E., J. Radio Anal. Chem. **1**, 169 (1968).

NEUTRON ACTIVATION ANALYSIS OF BARNACLE SHELLS

C. M. Gordon and R. E. Larson

Naval Research Laboratory
Washington, D.C.

I. Introduction

One of the current programs in our laboratory is a study of the influence of ecological factors on the elementary composition of marine invertebrate shells. The work presented here concerns the effect of salinity on the deposition of calcium, manganese, magnesium, strontium and sodium in barnacle shells. The technique employed in this investigation is radioactivation with reactor neutrons and computer analysis of the resultant gamma-ray spectra. The gamma-ray spectrometer consists of a Ge(Li) detector in combination with a 4096 channel pulse-height analyzer. Two computer programs have been written to process data from this instrument. The programs, written in Fortran for the CDC 3800 computer, were designed to duplicate, as nearly as possible, the results obtained when processing the data manually. The gamma-ray spectra are read from paper tapes. Additional information such as the number of spectra, energy calibration and times, is supplied with the programs on punched cards.

II. Experimental

Samples of marine animal shells of approximately 100 mg each are cleaned, dried and exposed to reactor neutron flux the order of $10^{13} n \cdot cm^{-2} \cdot sec^{-1}$. A three minute irradiation time has proved satisfactory for the isotopes of interest: ^{49}Ca, ^{56}Mn, ^{27}Mg, ^{87m}Sr and ^{24}Na; 512 channel gamma-ray spectra of the samples are measured 5 to 20 minutes following neutron activation and again about 2 hours later.

In cases when the samples have unknown composition, the gamma-ray spectra are analyzed using our program designated SCANTAPE. In this program the computer scans the spectra and compares possible peaks with local background to determine whether they are statistically significant. Peaks are classified as possible, probable, and definite. The program takes into consideration the possibility of a peak on a slope or a peak with a jagged top due to low count rate. A subroutine is called to compute the area under the photopeak and subtract the background. Well defined peaks are fit to a Gaussian distribution using the method of Zimmermann [1]. From this fit the midpoint is established. The midpoints of other peaks are located using the three highest points and the equation

$$X = X_o + (b\text{-}c)/(a\text{-}c) \tag{1}$$

where X_o is the highest channel and (a,b,c) are the (highest, next, and lowest) counts. The (+) is used if the second highest count (b) is in channel $X_o + 1$. The energy is computed from the equation

$$E(x) = A + BX + CX^2. \tag{2}$$

This program requires about 6 minutes to analyze 8192 channels of spectral data.

Neutron activation analysis for particular known isotopes in the marine biological samples is accomplished using a second program, PEAKAREA, which was specfically written for this purpose. Spectra of eight samples are recorded, once shortly after irradiation and again several hours after irradiation. The program analyzes gamma-ray peaks corresponding to Ca, Sr, Mn-Mg, and Na. Punched card data input includes approximate peak location, the half lives of the peaks, and the time after irradiation when each spectrum was recorded. The area under each peak is computed and corrected to the time of removal from the reactor. In the case of Mn-Mg, which have unresolved gamma rays at .85 MeV, the area under the peak of the late run (Mn) is used to calculate the Mn contribution to the Mn-Mg peak in the early run. The remainder (Mg) is used to compute the Mg at the time of removal from the reactor. The Sr/Ca, Mg/Ca, Mn/Ca and Na/Ca ratios in each sample are found. The average ratios and the average deviation in the ratios are then computed. The final printout is in tabulator form.

III. Results and Discussion

A. Results

The technique described has been used to study Ca, Sr, Mg, Mn and Na in the shells of barnacle species collected from various sites along the shore of Chesapeake Bay (Fig. 1). Since the water in this estuary has a broad salinity gradient (Fig. 1) and a relatively small temperature gradient it is particularly suitable for an investigation of the ecological effects of salinity on shell composition.

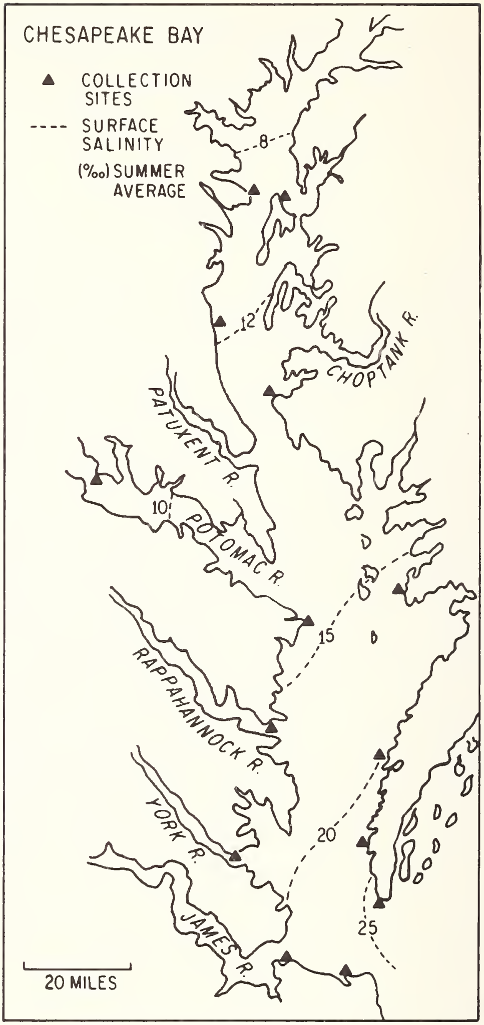

Figure 1. Barnacle collection sites.

Initial results indicate that manganese in the element most strongly correlated with salinity (Table 1). As is seen from the table, the manganese content in barnacle shells generally varies inversely as the salinity of the aquatic habitat.

It was also noted that variations in the manganese content of barnacles from the same salinity environment were considerably larger than could be accounted for by errors in the measurement technique. It is this variation that is reflected in the errors quoted in the table. The salinity

Table 1. Relative $^{55}Mn/^{48}Ca$ ratios in barnacle shells as a function of salinity.

Salinity	Barnacle species		
(⁰/oo)	*B. improvisus*	*B. eburneus*	*C. fragilis*
7	3.7 ± 1.0		
8.5	5 ± 1.0		
10	3.7 ± 1.3	.7 ± .4	
12	1.3 ± .7	.33 ± .02	
13	.37 ± .2	.17 ± .03	
14	.38 ± .2	.15 ± .08	
16	.19 ± .2	.12 ± .01	
17	.30 ± .2		.14 ± .04
19	.40 ± .2	.25 ± .06	.13 ± .03
20	.36 ± .2	.20 ± .03	.10 ± .02
22	.52 ± .2	.14 ± .03	.09 ± .02
26			.05 ± .01

values cited in the table are those measured at the time of collection, but it should be noted that in the estuarine conditions of this experiment the salinity at a given location may vary considerably over the lifetime of a barnacle.

In the case of one species, *Balanus eburneus* Gould, the data in Table 1 confirm in greater detail the limited results of Pilkey and Harriss [2], who found excess Mn in this species taken from brackish water near Sapelo Island, Georgia. The effect of salinity is even more pronounced in *Balanus improvisus* Darwin in which Mn in the shell may vary a factor of 10 with a relatively small change in salt content of the habitat.

It is also seen from Table 1, that the Mn:salinity relationship is nonlinear in the cases of *B. improvisus* and *B. eburneus*, with the Mn content increasing rapidly as salinity is reduced below about 13⁰/oo but relatively constant above this value. The species *Chthamalus fragilis* Darwin exhibits an analagous Mn:salinity trend in the salinity range where it was found but no nonlinear "threshold" effect has been noted.

The present work indicates that this inverse Mn:salinity relationship may apply to barnacles in general. However, our data also show large interspecific differences in the value of the Mn/Ca ratio for a given environmental salinity. For example, for four of the species studied: *C. fragilis, B. eburneus, B. improvisus* and *B. balanoides*, the relative manganese content was found to be 1, 1.8, 4.2, and 6.6, respectively, for a sample of animals living under the same salinity conditions at about 19⁰/oo.

No measurable correlation between strontium concentration and salinity has been observed in our samples. This result is in general agreement with studies made of salinity effects on Sr content in other animals [3,4], but no comparable data on barnacles are available in the literature.

In some of the species studied, magnesium and sodium are correlated with salinity; sodium positively and magnesium negatively. These correlations, however, are much weaker than in the case of manganese and further investigations on the details of these relationships are being conducted.

B. DISCUSSION

The trace element content of modern and fossil marine animal shells has been widely used as a clue to the chemical and physical parameters of the ancient environments where these animals lived. Many tentative conclusions have been drawn from these data regarding the biogeochemical cycles of specific elements [5,6] and the geological history of the oceans [7,8].

Our data on salinity effects in barnacles confirms the potential usefulness of this technique as a paleoecological tool but implies that inferences made on the basis of trace element ratios in fossil barnacles are of questionable value unless compared to contemporary animals of the same species.

IV. References

[1] Zimmerman, W., Rev. Sci. Inst. **32,** 263 (1965).
[2] Pilkey, O. H., and Harriss, R. C., Limnol. Oceanog. **11,** 381 (1966).
[3] Dodd, J. R., Geochim. et Cosmochim. Acta **29,** 385 (1965).
[4] Pilkey, O. H., and Hower, J., J. Geol. **68,** 203 (1960).
[5] Chave, K. E., J. Geol. **62,** 266 (1954).
[6] Odum, H. T., Science **114,** 407 (1951).
[7] Bowen, H. J. M., J. Mar. Biol. Asso. U. K. **35,** 151 (1965).
[8] Lowenstam, H. A., J. Geol. **69,** 241 (1961)

SAMPLING METHODOLOGY DEVELOPMENT IN A LARGE SCALE CYSTIC FIBROSIS SCREENING PROGRAM BASED ON AUTOMATED NEUTRON ACTIVATION ANALYSIS

L. E. Fite, R. E. Wainerdi, and H. P. Yule

Activation Analysis Research Laboratory
Texas A & M University
College Station, Texas 77843

G. M. Harrison, G. Bickers, and R. Doggett

Cystic Fibrosis Care, Teaching and Detection Center
Texas Institute for Rehabilitation and Research
Texas Medical Center
Houston, Texas 77025

I. Introduction

Cystic fibrosis (C/F) is the most serious nontubercular respiratory disease found in children today, and the need for a highly efficient and reliable method for the detection of cystic fibrosis in newborn infants is widely recognized. Only by early detection and improved pulmonary and dietary management can a signficant number of youngsters born with the disease survive to late adolescent and adult life [1].

One of the most reliable procedures for the detection of C/F is the sweat test [2], in which the sodium, chlorine and potassium concentrations observed in C/F patients has been found to be two to five times the concentrations found in normal individuals. However, immediately following birth, the sweat glands are inactive, and such a test cannot be used as a screening method to detect C/F in newborn infants.

The work of Kopita and Schwachman [3-5] indicates the possible use of the sodium concentration in fingernails as an indicator for the detection of cystic fibrosis in children and in newborn infants. Early work on the possible application of thermal neutron activation analysis has been done by Babb *et al* [6] and Andersen *et al* [7]. The large automated activation analysis systems designed and built at Texas A&M under United States Atomic Energy Commission-Division of Isotopes Development sponsorship have been applied to this investigation.

Since January, 1968, nail clippings taken from 713 individual newborn infants have been analyzed for sodium using the Mark II Automatic Activation Analysis System [8] as part of a joint Texas A&M/Baylor University College of Medicine research program. Of these, 160 samples have been re-analyzed to check the reproducibility of the technique and to verify the original results. A number of problems in sampling and sample preparation have been observed.

II. Experimental Procedure

A. Sample Collection

Nail clippings were obtained from newborn infants (birth to 48 hours) at Jefferson Davis and St. Luke's Episcopal Hospitals in Houston, Texas. Surgical scissors were used for clipping the nail samples. The scissors were previously washed with distilled water and wiped dry with cotton sponges. Clippings were taken from each finger (when possible) to provide a sufficiently large sample for analysis. The nurses taking the samples wore disposable plastic gloves and the clipped nail samples were handled with forceps to reduce the possibility of sample contamination.

The samples were packaged in small plastic vials and forwarded to the Texas A&M Activation Analysis Research Laboratory for analysis.

B. Sample Preparation for Irradiation

The samples were removed from the plastic vials in which they were shipped and weighed on a semi-microbalance. Typical total sample weights were 1-3 mg, although one sample weighed only 0.2 mg. The samples were identified by the patient's name, hospital number, and the date on which the sample was taken. The samples were handled with forceps and encapsulated in polyethylene vials which had been marked with a code number corresponding to one of the storage positions in the automatic activation analysis system.

Standard solutions containing known quantities of sodium were prepared and irradiated at the same time as the nail clippings to serve as reference standards. Reagent grade sodium carbonate and sodium oxalate were dried to a constant weight and weighed into a volumetric flask and diluted with de-ionized water. The standard solution contained approximately 5 μg/ml of Na. One ml of the solution was pipetted into a polyethylene vial and heat sealed to obtain a typical standard.

C. Irradiation

The samples were irradiated in a rotisserie at the Texas A&M University Nuclear Science Center Reactor, for 4 hours at a thermal neutron flux of $5 \times 10^{11} n \cdot cm^{-2} \cdot sec^{-1}$. The irradiations were usually performed in the evening of the day that the samples were received.

D. SAMPLE TRANSFER

Following activation, the rotisserie containing the samples and standards was returned to the AARL and unpacked. To eliminate ^{41}Ar contained in air and ^{24}Na contamination in the vials, it was necessary to transfer the nail sample to nonirradiated polyethylene vials for counting.

E. COUNTING

The Mark II automatic activation analysis system was used to count the samples and standards. The system consists of three gamma-ray spectrometers, *i.e.* three 3 in. × 3 in. NaI(Tl) crystals and three 400 channel pulse-height analyzers with digital gain and baseline stabilization, two sample storage libraries, a pneumatic transfer system, a real time clock, a computer compatible magnetic tape readout and a control system.

The samples located in the storage library are selected automatically by the control system and transferred to one of the detectors *via* the pneumatic tube. When the count starts the time is recorded to the nearest 0.01 minute on magnetic tape along with the sample identification number and the analyzer code number. The analyzer code number is used by the computer to determine which samples were counted by each pulse-height analyzer. At the end of the counting period, the time as well as the data stored in the memory of the pulse-height analyzer is recorded on the magnetic tape. This system is fully described elsewhere [9].

The sodium standards are counted on all three pulse-height analyzers to provide the computer with the standard sodium spectra necessary for the calculation of the relative mass of sodium in the nail samples. The typical counting time was two minutes. Since the three pulse-height analyzers count the samples independently and simultaneously, the nail samples are processed at the rate of 100 samples per hour.

While the samples were being counted on the Mark II system, IBM header cards were punched containing the sample identification number and the sample weights. With this additional information, the results obtained from the computer are expressed in parts per million (ppm) sodium.

After the samples had been counted and the data placed on computer compatible magnetic tape, the general purpose activation analysis computer program "HEVESY" [10], the magnetic tape, and the punched cards containing the sample weights were submitted to the Texas A&M IBM 360/65 computer for processing. After computing the yields of ^{24}Na for the 1.37 MeV and 2.75 MeV full energy peaks for each of the three detectors, the computer determines the ppm sodium for each of the nail samples.

The results of the analysis was usually obtained the following morning. After comparing the results of the standards containing known quantities of sodium the results were tabulated with the patient's name, hospital number and sample weight and returned to the hospital within 48 hours after the samples were received.

III. Results

The initial phase of this research effort involved the sodium analysis of nail clippings obtained from normal children and children known to have cystic fibrosis. The results are shown in Figure 1. As was expected, the sodium level observed in the nails from the known C/F cases is a least twice that found in the nails of normal children.

To determine the reliability and accuracy of the irradiation and counting procedures, 17 standard sodium samples were irradiated and counted by each of the pulse-height analyzers of the Mark II system. The results of this test are given in Table 1 and the sodium analysis was within seven percent of the known sodium concentration.

The reproducibility as a function of the variability in the same individual as a function of time is given in Table 2 wherein nail clippings from the laboratory staff were analyzed on three different occasions for

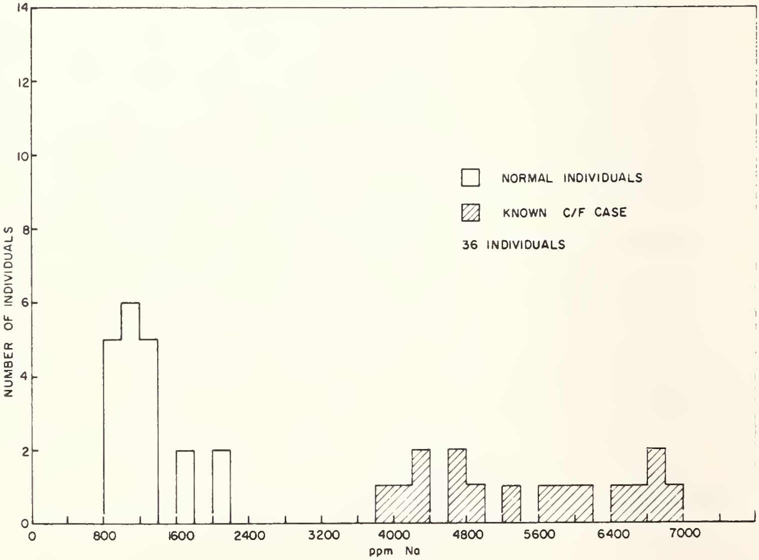

Figure 1. Sodium analysis of nail clippings from normal and known C/F individuals.

Table 1. Analysis of reference standards containing 8.5 μg sodium.

Sample number	Analyzer A	Analyzer B	Analyzer AB
	Micrograms of sodium		
4	8.45	8.35	8.24
5	8.62	8.03	8.81
6	8.70	8.51	8.66
7	8.83	8.91	8.41
8	8.33	8.27	8.13
9	8.42	8.26	8.06
10	8.26	8.58	8.81
11	8.67	8.55	8.23
12	7.96	8.24	7.99
13	8.51	8.91	8.45
14	8.11	8.49	8.54
15	8.58	8.49	8.87
16	8.69	8.07	8.47
17	8.38	8.70	8.34
18	8.16	8.66	8.23
19	8.83	8.81	8.57
20	8.58	8.44	8.04

Table 2. Repeated sodium analysis of adult nail clippings.

Sample number	Run 1	Run 2	Run 3
		Sodium (ppm)	
1	1020	1060	980
2	910	1000	950
3	700	740	715
4	740	710	750
5	1090	1180	1130
6	1190	1160	1170
7	1000	1050	1000
8	1200	1060	1040
9	1210	1180	1170
10	1025	1060	1070

their sodium content. The ppm sodium determined from the repeated analysis was within 10 percent.

The sodium analysis of 119 newborn infants from Jefferson Davis Hospital is shown in Figure 2. The average sodium content of the individual nail samples was 4285 ppm sodium. This is 2 to 3 times above the sodium level observed in older normal children 3 months to 12 years of age. Figure 3 shows the analysis of 76 infants born at St. Luke's Episcopal Hospital with an average of 3040 ppm Na. The sampling technique previously described was used by the nurses at both hospitals and the samples were intermixed when irradiated and analyzed.

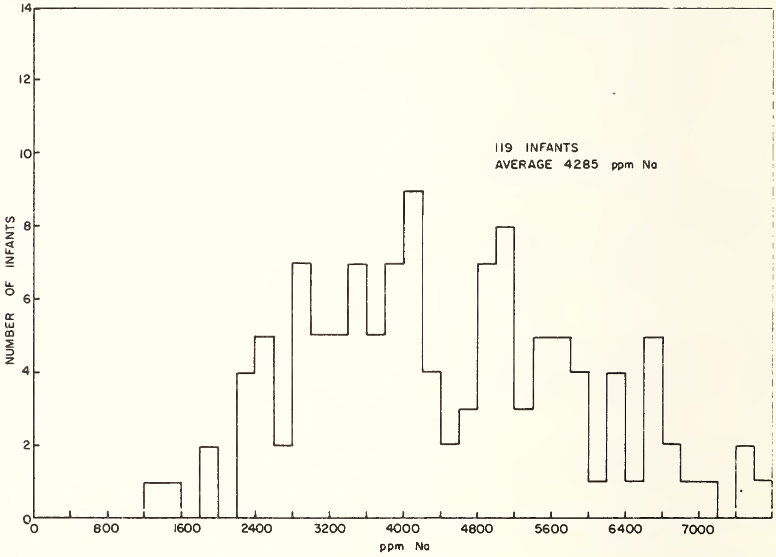

Figure 2. Sodium analysis of nail clippings from newborn infants at Jefferson Davis Hospital.

The high sodium level observed in the newborn infants' nails could result from the evaporation of the amniotic fluid which contains approximately 8000 ppm sodium or from contamination by meconium staining or from other sources. To determine the possibility of surface contamination, an experiment was initiated where the nails of one hand were washed in 95 percent ethyl alcohol and/or distilled water. The other hand was not washed before the nails were clipped. The results of this experiment clearly indicated surface contamination of the nail and the amount of sodium detected in the nail clippings of the washed hand was reduced. Both alcohol and distilled water had the same cleaning effect on the nail clippings. As a result of this experiment, before clipping it was

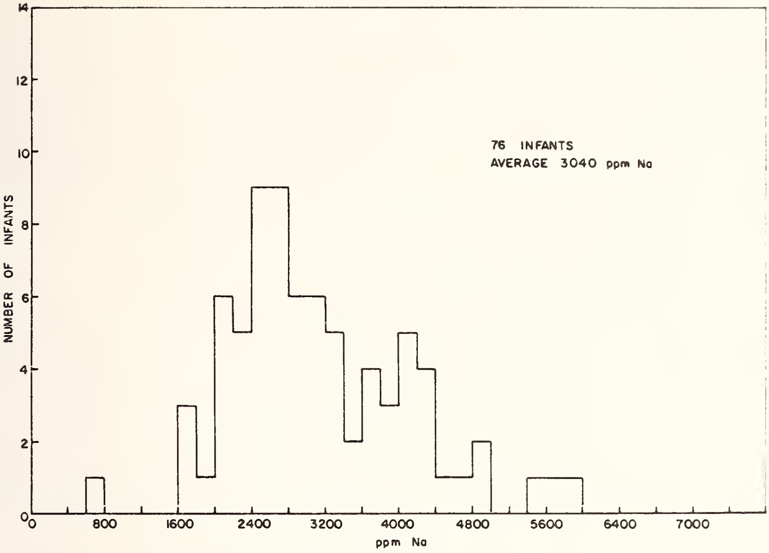

Figure 3. Sodium analysis of nail clippings from newborn infants at St. Luke's Episcopal Hospital.

decided to wipe the nails with a gauze soaked in alcohol because of the ease of application.

It was observed from the data accumulated during this study that (1) meconium staining of the nails tends to raise the sodium level of the analysis, and (2) the sodium level of the nail samples decreased rapidly with age of the infant up to 12 to 14 hours after birth as shown in Figure 4.

The routine sampling and sodium analysis of nail clippings from 127 newborn infants is shown in Figure 5. Of these 33 infants have a sodium level above 3600 ppm, and the possibility of contamination from meconium staining is being investigated. A sweat test and additional nail clippings are to be obtained from most of these infants at a later date. The general reduction in sodium level is evident when Figure 5 is compared with Figure 2.

The principal question remaining is whether or not the cleaning methods described above would cause a true C/F infant to be missed during the screening. While the experiments involving older children with C/F are encouraging, it is essential that these procedures be tested on newborn infants with C/F. Attention is being given to locating parents with a high expectancy of having a C/F child so that the dynamics of sodium transfer in the nail, and contamination removal can be studied in detail at birth and under circumstances comparable to those which have been employed in the study of normal infants.

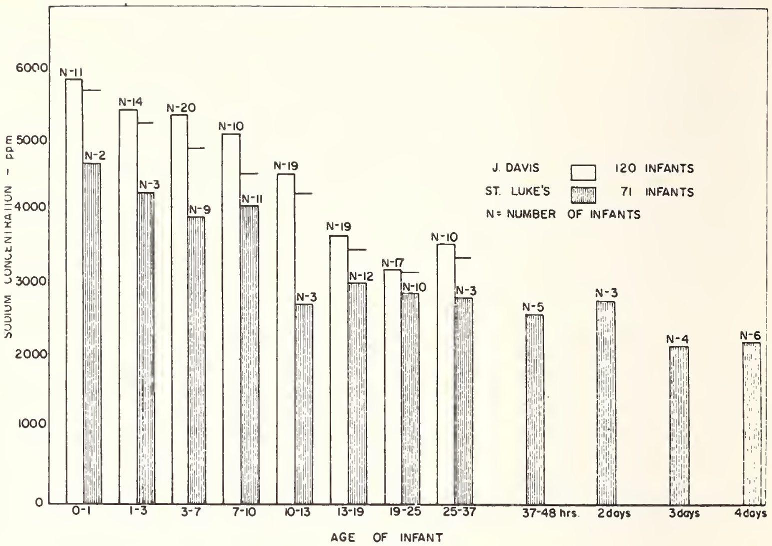

Figure 4. Sodium concentration in nail clippings as function of infant's age.

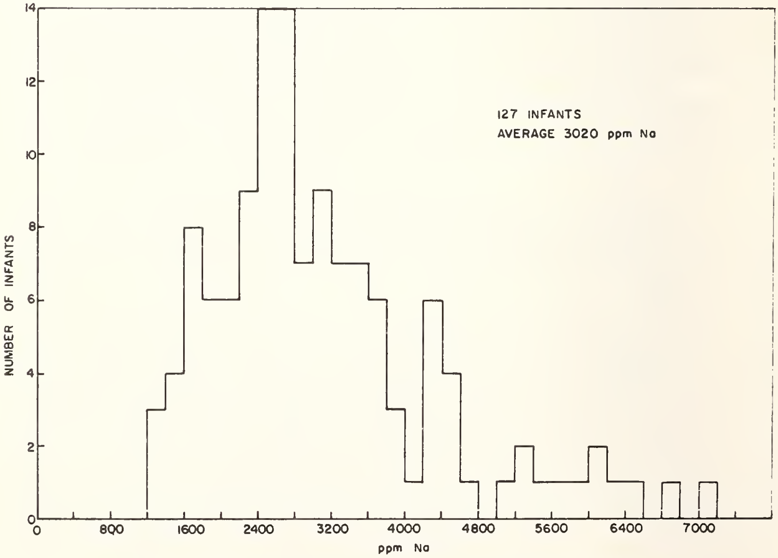

Figure 5. Routine sodium analysis of newborn infants fingernails.

IV. Acknowledgment

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V. References

[1] Harrison, G., Private Communication, 1968.

[2] Gharib, R., Joos, H. A., and Hilty, L. B., "Sweat Chloride Concentration", American Journal of Diseases of Children **109,** 66-68 (1965).

[3] Kopito, L., and Shwachman, H., "Spectroscopic Analysis of Tissues from Patients with Cystic Fibrosis and Controls", Nature **202,** 501 (1964).

[4] Kopito, L., and Shwachman, H., "Studies in Cystic Fibrosis-Analysis of Nail Clippings for Sodium and Potassium", New Eng. J. Med. **272,** 504 (1965).

[5] Shwachman, H., and Kopito, L., "Some Genetic Considerations in Cystic Fibrosis. A Study of Nail and Sweat Sodium in Two Sibships", Acta Paediatrica Scandinavica, Supplement **172,** 192-199 (1967).

[6] Babb, A. L., Woodruff, G. L., Wilson, W. E., Jr., Heintz, P. A., Miller, W. P., and Stamm, S. J., "The Use of Neutron Activation Analysis in the Early Diagnosis of Cystic Fibrosis in Children", Trans. Am. Nucl. Soc. **9,** 591 (1966).

[7] Andersen, G. H., and Gareis, F. J., "The Possible Detection of Cystic Fibrosis by Means of the Neutron Activation Analysis of Fingernails", Trans. Am. Nucl. Soc. **10,** 57 (1967).

[8] Investigations in Automated Activation Analysis, A&M College of Texas, Report TEES-2671-4 (1965).

[9] Wainerdi, R. E., Fite, L. E., Gibbons, D., Wilkens, W. W., Jimenez, P., and Drew, D., "The Design and Use of and Advanced, Integrated, Automatic System and Computer Program for Nuclear Activation Analysis", Radiochemical Methods of Analysis, Vol. II., International Atomic Energy Agency, Vienna, 149-159 (October 1964).

[10] Yule, H. P., Private Communication, 1968.

CLINICAL EXPERIENCE WITH THE USE OF NEUTRON ACTIVATION ANALYSIS IN THE DIAGNOSIS OF CYSTIC FIBROSIS

Gene L. Woodruff, William E. Wilson, Jr., Yuki Yamamoto, and Albert L. Babb

Department of Nuclear Engineering
University of Washington
Seattle, Washington 98105

Stanley J. Stamm

Children's Orthopedic Hospital and Medical Center
4800 Sand Point Way
Seattle, Washington 98105

I. Introduction

For the past two years the Department of Nuclear Engineering at the University of Washington and Children's Orthopedic Hospital and Medical Center of Seattle have cooperated in a program aimed at the development of a screening technique for cystic fibrosis [1,2]. The technique is based on the measurement of trace element concentrations in tissue samples from children. Previous work has indicated that abnormally high concentrations, notably sodium, can be correlated with diagnosis of cystic fibrosis (CF) [3]. The use of neutron activation analysis has significant advantages that offer the potential for a mass screening procedure of wide application. The present study was thus motivated toward the solution of the engineering problems of a successful screening process as well as the procurement of the data required for its success.

II. Experimental

Although samples analyzed have included hair and fingernails, the standard procedure currently in use is based on toenails. Samples are obtained through regional cystic fibrosis clinics throughout the U.S. following a rigidly prescribed procurement procedure. Batches of nails are irradiated for approximately thirty minutes in the University of Washington Nuclear Reactor and subsequently counted separately for beta and gamma radioactivity. Analysis of the data permits the routine determination of the concentrations of sodium, potassium and chlorine in nail samples weighing less than 0.1 mg; a sample size representative of those obtainable from newborn infants and smaller by a factor of about 200 than the minimum acceptable size required by other techniques [3]. The most controversial element of the procurement procedure is the washing; many of the same considerations are appropriate to trace element measurements in biological samples, in general.

Some sort of washing procedure is generally considered to be necessary in order to remove gross external contamination. Sodium in particular is very abundant in such common materials as table salt, soap, shampoo, hair oil, and sea water. Washing samples in the laboratory is objectionable for at least two reasons: (1) the additional steps required increase significantly the time and expense involved and thereby impair the feasibility of the method as a mass screening procedure; and (2) experience has shown that it is difficult to obtain a reproducible washing procedure that does not remove the "intrinsic" sodium (as contrasted with "contamination" sodium) to such an extent that the usefulness of sodium concentration as a criterion is somewhat compromised. On the other hand, washing prior to clipping nails offers the possibility of recovery to equilibrium. Tests have been made to confirm this in which a small piece of a nail has been clipped, the hand (or foot) soaked for twenty minutes, and then additional pieces clipped at intervals over the next few hours. Some results from such tests are shown in Figure 1. The results indicate that the washing immediately suppresses the sodium concentration to an abnormally low value but that over a period of about four hours, a gradual recovery to equilibrium is usually effected.

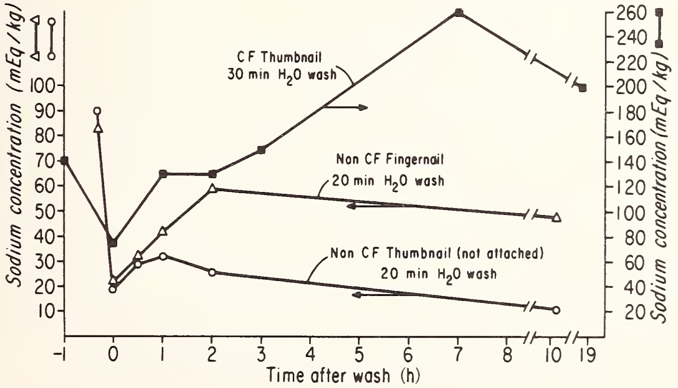

Figure 1. Time dependence of sodium concentration in nails following washing.

It should be noted that unplanned washes can introduce serious errors regardless of the washing procedure used. Samples from a group of children having cystic fibrosis consistently showed low sodium concentration until it was observed that this group was participating in an organized swimming program. After a protracted active session in the pool, a day or more may be required before equilibrium concentrations are re-established.

The feasibility of a mass screening process involving large quantities of data requires that automation be employed wherever possible. Counting of the samples is done on an automatic sample changer and results are then analyzed with digital computers. A computer card giving all the available pertinent information is kept for each sample.

III. Results and Discussion

Results obtained from the analysis of over 2000 samples lead to the following conclusions:

1. Measurements of sodium concentration alone are a useful supplement to other diagnostic results. Although the sweat test constitutes a very reliable diagnostic procedure, it cannot be performed on infants; it requires that the child be brought to a laboratory where experienced personnel are available, and it sometimes gives ambiguous results even when properly performed. In the present work, at least one infant has been diagnosed as having cystic fibrosis that would probably have escaped detection otherwise. It has also been observed, for example, that right heart failure in cystic fibrosis patients is accompanied by a sudden drop in nail sodium.

2. The measurement of sodium concentration alone is probably not sufficient as a basis for a successful screening technique. An empirical criterion of about 110 meq Na/kg nail provides an optimum boundary between controls and patients having cystic fibrosis when the procedure described above is used (except for infants which are a special category). A screening test based on this procedure along would require follow-up sweat tests in 15-30% (depending on the washing procedure) of the cases analyzed. This is an unacceptably high percentage of false positives.

3. The measurement of sodium:potassium concentration ratios is helpful in detecting false positives caused by gross external sodium contamination. The concentration of potassium is also elevated in samples from CF patients, and there is no apparent correlation between sodium contamination and potassium contamination. Sodium:potassium ratios in excess of 4 are indicative of contamination. Use of this rejection criterion reduces the false positives by a factor greater than 2.

4. The source of the sodium contained in fingernails (and presumably toenails as well) is the sweat glands located immediately beneath the nails. Tests were made of the time dependence of the sodium concentration following washing of two nails on the same hand. One nail was normal, the other, as a result of an accident, was not in contact with the underlying tissue. As shown in Figure 1, the former recovered to equilibrium within a few hours while the latter still had not recovered ten hours later.

5. Sodium concentration in nails varies with age and the variation is strongest in the first few days of life. Sample procurement from infants involves additional complications, not all of which have been resolved. It is nonetheless clear that sodium concentrations are at a maximum at the time of birth and are a monotonically decreasing function of age, thereafter. Decreases of more than a factor of 2 within the first 72 hours are not uncommon.

IV. Acknowledgment

The assistance of Patti Polinsky and W. P. Miller in the nail procurement and analysis is gratefully acknowledged.

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V. References

[1] Babb, A. L., Woodruff, G. L., Wilson, W. E., Heintz, P. H., Miller, W. P., and Stamm, S. J., "The Use of Neutron Activation Analysis in the Early Diagnosis of Cystic Fibrosis in Children", Trans. ANS **9**, 591 (1966).

[2] Heintz, P. H., "The Application of Neutron Activation Analysis to Cystic Fibrosis Detection", M.S. Thesis, University of Washington (1967).

[3] Kopito, L., *et al,* "Studies in Cystic Fibrosis Analysis of Nail Clippings for Sodium and Potassium", New Eng. J. Med. **272,** 10, 504 (1965).

ACTIVATION ANALYSIS IN PLANT BIOLOGY. RADIOECOLOGICAL APPLICATIONS USING SIMPLE OR AUTOMATED RADIOCHEMICAL SEPARATION TECHNIQUES

A. Fourcy, M. Neuburger, C. Garrec, A. Fer, and J. P. Garrec

Laboratoire de Biologie Vegetale du Centre d'Etudes Nucleaires
de Grenoble, B.P. 269
38 – Grenoble, France

I. Introduction

Increasing development of geochemical ecology in plant biology, connected with better sensitivity of analytical methods depends on two facts: the increasing interest for trace elements in the life sciences and the need for larger radioecological studies.

Let us develop the second point. In health physics it is necessary to follow the behavior in environment and the concentration in food chain of radioactive wastes. Radioelements constituting wastes have their corresponding stable nuclides in the environment, and except for fall out, radionuclides are generally isotopically "diluted" in natural stable elements. This remark explains the interest in analyzing total content of plants for Ru, Fe, Co, Zn, Na, K, Rb, Cs, Ca, Sr, Sc, Ba, and some rare earth elements. The above elements have been chosen for their radioecological interest and their ability to be analyzed by radioactivation.

Some authors have used plant analysis for trace elements in radioecological studies. Among the most recent papers, one finds Jaakola, *et al* [1] working with chemical methods rather than activation analysis, thinking the latter one too long; Kirchmann, *et al* [2] comparing atomic absorption and activation analysis for strontium, Merlini, Girardi and Pozzi [3] using an instrumental method of activation analysis with Ge(Li) detectors. We have previously described the general advantages of activation analysis in radioecology [4]. We propose here a general method using semi-automated radiochemical separations after radioactivation and NaI(Tl) detection. Advantages are selectivity, sensitivity and the number of elements simultaneously determined. A compromise is realized between these advantages and a reduction of the time for each analysis.

Besides the analysis of natural elements in the environment, we have applied activation analysis to experiments consisting of an enrichment in stable elements, like Ru or Cs, of an aquatic ecosystem to study the partition of them in water and plants.

II. Experimental

A. Apparatus and Reagents

Activation analysis for trace elements with NaI(Tl) scintillation detectors usually needs radiochemical separations. Two methods are used: (1) Distillation for ruthenium, since it is a relatively simple process to obtain this element [5,6], and (2) Ion exchange for other elements, since automation in resin chromatography is feasible.

1. Distillation Device

It consists of a very simple glass apparatus represented in Figure 1.

2. Ion Exchange

An automated apparatus has been built in the laboratory for sequential elution on 8 columns, simultaneously. Eluting solutions are distributed at the proper time by electric peristaltic valves and are pushed through the column by a peristaltic pump. Fractions are collected on a rotating plate synchronized with the change of solutions, Figure 2.

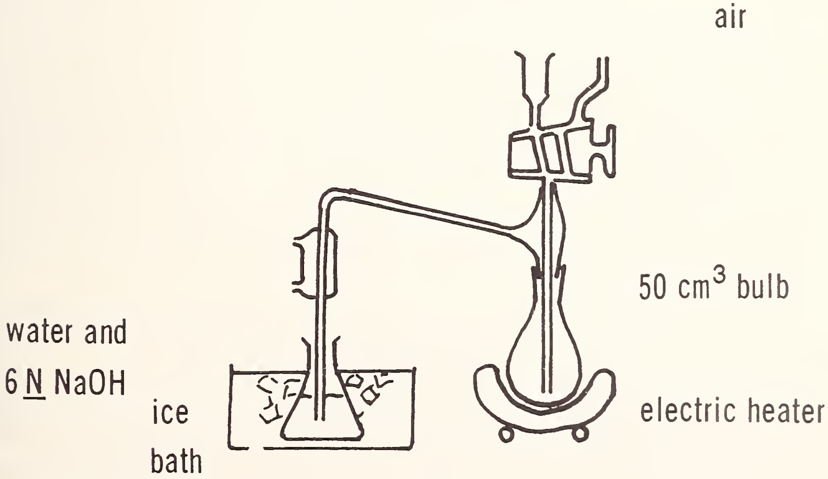

Figure 1. Distilling apparatus scheme.

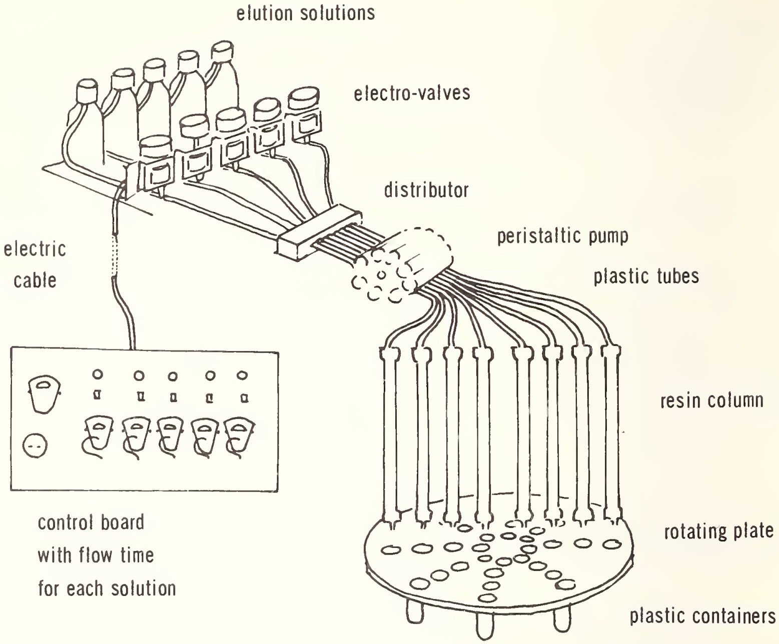

Figure 2. Automated system for sequential elution.

B. Procedure

1. *Distillation of Ru*

After an irradiation of 120 h in a thermal flux of $2 \times 10^{13} \text{n} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$ and convenient radioactive decay (one week), introduce a quartz capsule containing the sample into the glass bulb (Fig. 1). Add 2 ml of 36 *N* sulfuric acid and 0.5 ml of a carrier Ru solution at 10 mg/ml. Heat gently. Vapors are caught in an Erlenmeyer flask filled with 6 *N* NaOH. A slow air flow regulates the process.

When the sample is extracted from the capsule, add 10 ml of perchloric acid $HClO_4$ and 0.5 g of sodium bismuthate $NaBiO_3$. Ruthenium is then oxidized to RuO_4 which is rapidly distilled at 130°C. After seeing yellow RuO_4 vapors distill for 10 minutes more to be sure that the radiochemical separation is quantitative. To optimize gamma counting of ^{103}Ru ($T_{1/2} = 40$ d) wait for some days decay of ^{82}Br ($T_{1/2} = 35.9$ h). The gamma spectrum for ruthenium fraction is shown in Figure 3.

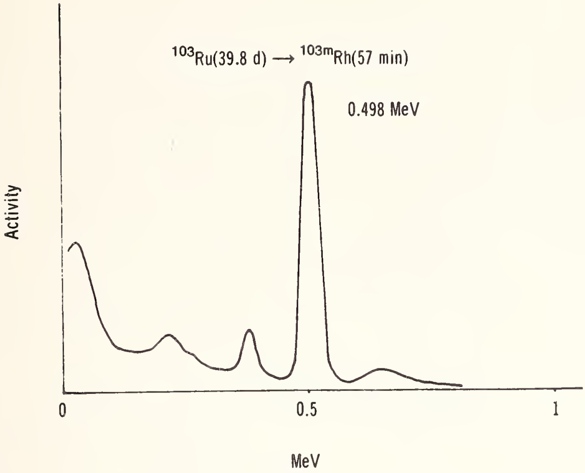

Figure 3. Gamma spectrum of the distillated fraction obtained from a sample of *Potamogeton natans* on a ruthenium enriched water.

2. *Ion Exchange*

Plant samples are dry ashed. After an irradiation of 5 days in a thermal flux of 10^{13} $n \cdot cm^{-2} \cdot sec^{-1}$, sample ashes are dissolved in strong acids (*e.g.* HNO_3 and some drops of H_2SO_4). Oxidation is completed by H_2O_2 and the residue is taken back into 8 *N* hydrochloric acid.

The radiochemical separation is divided in two phases. One is passing the solution through a Dowex 1.10, 200 × 400 mesh resin in 8 *N* HCl to retain and separate Co, Fe and Zn (Fig. 4, left). The first eluated fraction containing P and many other elements is dried and dissolved in O.1 *N* HCl for a new fixation on Dowex 50W, 200 × 400. Then, the following elements are eluated: P, Na, K, Rb, Cs, Mn, Ca, Sr, Sc, rare earths (from Yb to La) and Ba (Fig. 4, right). The radionuclides used are listed in Table 1.

III. Results and Discussion

A. Results

1. *Ruthenium*

Sensitivity of the method as calculated by gamma counting at 100 counts per minute is 3.10^{-3} μg with a 4 in. × 4 in. NaI well crystal.

As the natural level of stable ruthenium is negligible in the ground of the Nuclear Center, we have used Ru as an enrichment of an experimental

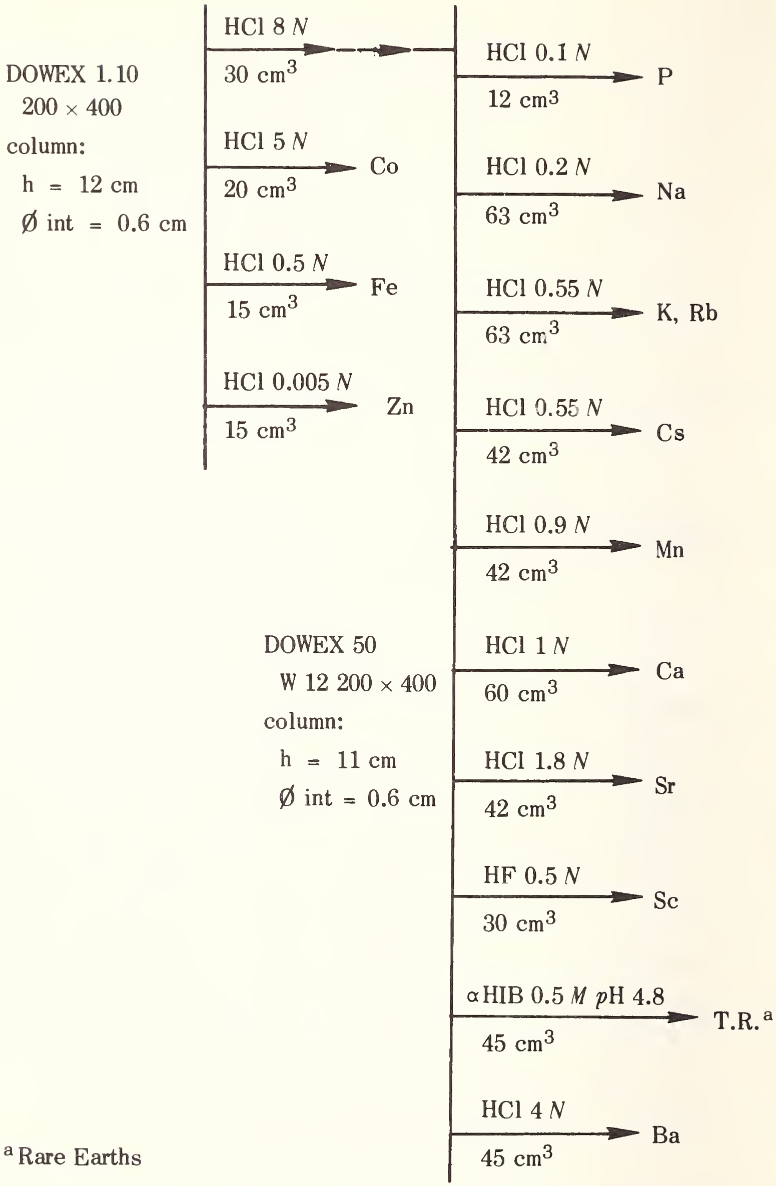

Figure 4. Ion exchange scheme for radioecological studies.

pond. In a 60 m² aquatic ecosystem, we have introduced a small amount of ammonium aquochlororuthenate $(NH_4)_2(RuH_2OCl_5)$ so that the theoretical initial concentration would be 0.0538 parts per million (ppm) in water. This concentration was sufficient to observe the partition of

Table 1. Radionuclides used in the ion exchange process.

		Half life	γ rays in MeV	Interferences[a]
Na	$^{23}Na(n, \gamma)^{24}Na$	15 h	1.38 2.76	$^{24}Mg(n, p)^{24}Na$
K	$^{41}K(n, \gamma)^{42}K$	12.5 h	1.52	$^{42}Mg(n, p)^{42}K$
Rb	$^{85}Rb(n, \gamma)^{86}Rb$	18.6 d	1.08	$^{86}Sr(n, p)^{86}Rb$
Cs	$^{133}Cs(n, \gamma)^{134}Cs$	2.1 y	0.60	$^{134}Ba(n, p)^{134}Cs$
Ca	$^{46}Ca(n, \gamma)^{47}Ca$	4.7 d	1.30	
Sr	$^{84}Sr(n, \gamma)^{85}Sr$	64 d	0.51	
Sc	$^{45}Sc(n, \gamma)^{46}Sc$	84 d	1.12	$^{46}Ti(n, p)^{46}Sc$
La	$^{139}La(n, \gamma)^{140}La$	40.2 h	1.60	$^{140}Ce(n, p)^{140}La$
Ba	$^{130}Ba(n, \gamma)^{131}Ba$	11.5 d	0.496	

[a] Usually negligible.

total Ru and uptake by aquatic plants: *Alisma plantago, Potamogeton natans, Baldingera arundinacea.* See Table 2 and Figure 5.

2. *Other Elements*

Table 3 gives for each element analyzed the practical sensitivity of the method for convenient use in radioecology. Two types of experimentation have been made. One provides for a detailed analysis of plants and water for trace elements of the fission product family. Table 4 gives the content in Sr and Cs of some aquatic samples. The other is an experiment consisting of an introduction of low amounts of cesium (enrichment) in a closed ecological system. As an example of the method, evolution of Cs concentration by a plant as measured by radioactivation is given in Figure 6.

B. DISCUSSION

The distillation process for ruthenium of biological samples is a very rapid and convenient means to obtain a fraction ready for gamma spectrometry. Ion exchange is a longer way to treat plant material, but in regard to time, the number of simultaneous dosages must be considered.

Table 2. Ruthenium content in the water of an ecological pond.

Elapsed time after enrichment by Ru	Ru water content in μg/l (ppb)
30 min	2.05
1 h	6.13
1 h 30 min	3.27
2 h 30 min	5.76
3 h 30 min	2.43
4 h 30 min	0.97
5 h 30 min	0.38
23 h	0.36
3 days	0.27
6 days	0.67
9 days	0.14
29 days	0.22
56 days	0.18

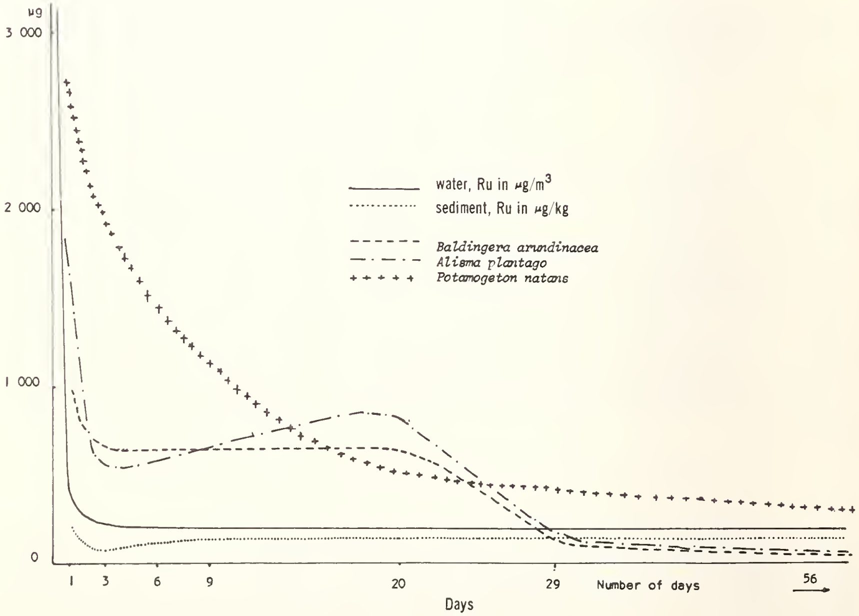

Figure 5. Ruthenium concentration in a plant aquatic ecosystem, after an enrichment in ammonium aquochlororuthenate. (Results in μg/kg of dry matter.)

Table 3. Sensitivity observed for some elements with the proposed method. (Experimental sensitivity after a 5 days irradiation and a 4 days decay.)

Element	Radioisotope	Sensitivity (μ g/g)	Average amount in plant (μ g/g)
Fe	^{59}Fe	1.3	200
Co	^{60}Co	0.03	0.2
Zn	^{65}Zn	0.14	30
Na	^{24}Na	0.1	82
K	^{42}K	1	14,000
Rb	^{86}Rb	0.1	10
Cs	^{134}Cs	2.5×10^{-3}	0.15
Ca	^{47}Ca	66	16,000
Sr	^{85}Sr	1	30
Sc	^{46}Sc	2×10^{-4}	0.12
La	^{140}La	1.4×10^{-3}	0.4
Ba	^{131}Ba	0.3	10

Table 4. Strontium and cesium content of some aquatic plants of Grenoble.

Plant	Sr (μ g/g)	Cs (μ g/g)
Baldingera arundinacea	34	0.40
Potamogeton natans	154	0.33
Alisma plantago	79	0.23
Chara sp.	502	0.76

In a previous work [7], we had used gradient elution by HCl. Elements were collected in many small tubes. Each fraction had to be identified by gamma spectrometry, combined with those of similar content, and finally counted for one element. To avoid that we have improved the sequential elution in order to collect elements as a whole in one fraction (Fig. 4).

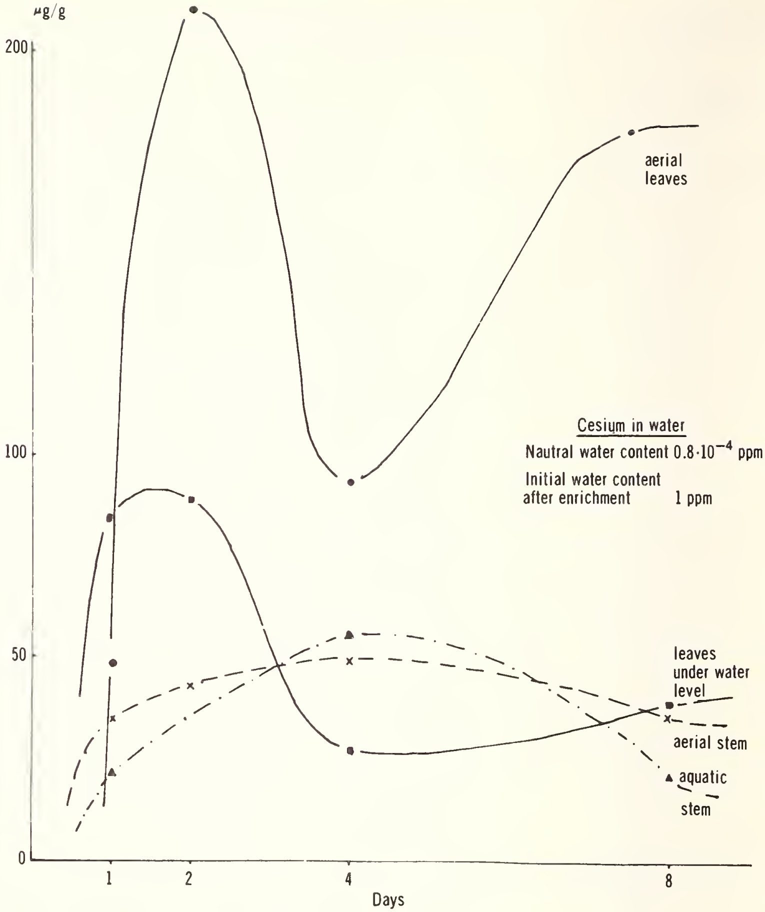

Figure 6. Cesium concentration in *Baldingera arundinacea* as measured by radioactivation after enrichment of water.

C. CONCLUSION

Activation analysis is a very vital tool for radioecology, and permits analyses of stable elements in the environment which corresponds to radionuclides of radioactive wastes. It remains a rather fastidious method if not automated [1]. That is why the first step in this work attempts greater use of automated radiochemistry, making activation analysis a fine tool for geochemical ecology.

IV. References

[1] Jaakola, T., Poumala, H., and Miettinen, J. K., Radioecological Concentration Processes, Pergamon Press, Stockholm, 1966.

[2] Van Puymbroeck, S., Jacquemin, R., Colard, J., Kirchmann, R., and Van der Borgat, O., Nucl. Act. Meth. in Life Sciences, IAEA, Vienna, 1967.

[3] Merlini, M., Girardi, F., and Pozzi, G., Nucl. Act. Meth. in Life Sciences, IAEA, Vienna, 1967.

[4] Fourcy, A., Fer, A., Poret, C., Neuburger, and Garrec, J. P., Bull. Inform. Scient. et Techn. du C.E.A. **119,** 1 (1967).

[5] Wyatt, E. J., and Richard, R. R., NAS-NS 3029, Rep., 1961.

[6] Thiers, R., Graydow, W., and Beamish, F. E., Anal. Chem. **20,** 9, 831 (1948).

[7] Fourcy, A., Fer, A., Barbe, R., and Neuburger, M., Isotopes in Plant Nutrition and Physiology, I.A.E.A., Vienna, 1967.

DETERMINATION OF VANADIUM BY NEUTRON ACTIVATION ANALYSIS AT NANOGRAM LEVELS IN DIETS FOR EXPERIMENTAL ANIMALS

J. P. F. Lambert and R. E. Simpson

Food and Drug Administration
Washington, D.C. 20204

I. Introduction

To study the significance of trace amounts of vanadium in animals and man, an ultra-sensitive analytical method for determining this element is required. In a biological study on vanadium, Schroeder *et al* [1] used a colorimetric method which is reliable at microgram levels, for samples of 10-100 g. However, a major limitation in their method is the relatively high background level of vanadium found in chemical reagents required in the isolation of the element. Neutron activation analysis (NAA) eliminates this limitation and the separation of vanadium is enhanced by the use of a "vanadium carrier" in the chemical separation procedure. Wahl *et al* [2] used NAA to determine microgram levels of vanadium in ore samples. In their method pulverized ore samples were exposed to a high flux of thermal neutrons. Following the exposure, the samples were fused and the vanadium separated by solvent extraction. The ^{52}V produced by the ^{51}V(n,γ)^{52}V reaction was analyzed by gamma-ray spectroscopy.

This paper presents an evaluation of the NAA method for determining vanadium at nanogram levels and its application to the survey of vanadium in animal diets and in individual diet ingredients. These results were used to select constituents low in vanadium for the preparation of a "vanadium-free" animal diet. This diet is being fed to experimental animals to study the significance of trace levels of this element in biological systems.

II. Experimental

A. APPARATUS AND REAGENTS

Gamma-ray spectrometer. A 3 in. × 3 in. NaI(Tl) crystal with a 0.65 in. × 2 in. well, and a 256 channel pulse-height analyzer calibrated at 10 keV per channel was used.

Vanadium standard solution, 100 μg/ml. Dissolve 0.2296 g of reagent grade ammonium metavanadate in distilled water and dilute to 1000 ml. Prepare appropriate dilutions for irradiation as needed.

Vanadium carrier solution, 1 mg/ml. Dissolve 3.9 g of reagent grade vanadyl sulfate in distilled water and dilute to 1000 ml.

n-Phenylbenzohydroxamic acid reagent. Prepare a 5% solution in chloroform.

Potassium permanganate reagent. Prepare a 7% solution in distilled water.

B. PROCEDURE

Handle samples in accordance with the nature of the material to be analyzed. For dietary materials included in this work, proceed as follows: char approximately 40 g of water insoluble solid samples at 400 °C and ash at 650 °C in a muffle furnace.

Place up to 500 mg of an ash or a solid in a clean 1 ml polyethylene snap-cap vial; or, place 1 to 4 g of a liquid sample in a 1 or 5 ml polyethylene snap-cap vial. Transfer 1 ml of vanadium standard to a separate vial of the size used for the sample. Expose both sample and standard simultaneously for 4 minutes in a nuclear reactor to a thermal flux of $10^{13}\text{n}\cdot\text{cm}^{-2}\cdot\text{sec}^{-1}$. After irradiation transfer the sample to a 150 ml beaker. Rinse the exposure vial with 1 ml of vanadium carrier followed by 1 ml of water. Add the rinsings to the sample in the beaker. Dilute the sample solution to approximately 10 ml with water and add 1 ml of the potassium permanganate reagent to oxidize all the vanadium to the +5 valence state. Add concentrated hydrochloric acid to make the solution 5 to 9 *M*. Apply heat, as needed, to completely dissolve all solids. Cool the solution in an ice bath. Quantitatively transfer the solution to a 125 ml separation funnel. Extract the vanadium by shaking the solution vigorously with 10 ml of the n-phenylbenzohydroxamic acid reagent. Transfer the chloroform layer to a 16 mm × 125 mm test tube. Insert the test tube into the well of the NaI(Tl) crystal. Count for 2 minutes recording the sample's gamma-ray activity in all 256 channels.

Transfer the vanadium standard to a beaker containing unirradiated sample or ash equivalent to the irradiated sample. Process in the same manner as the irradiated sample.

Determine the vanadium content in the sample by comparing the net integrated count under the 1.43 MeV photopeak of the ^{52}V in the sample with that recorded for the vanadium standard.

III. Results and Discussion

A. SENSITIVITY

At nanogram levels of vanadium, the chemical separation time is a key factor in the sensitivity of the method. In using the present procedure an average separation time of approximately 7 minutes for ashed samples and 4 minutes for liquid or water soluble samples has been achieved. In view of the 3.77 minute half life of ^{52}V a factor of two loss in sensitivity occurs for every half life used for the separation.

To determine the maximum sensitivity of the method, water samples containing known amounts of vanadium were analyzed. The recoveries of vanadium are given in Table 1. Good recoveries were realized down to a level of 3.2 ng of added vanadium. Although theoretical calculations indicate a sensitivity limit of 0.3 ng, the recovery for the sample with 0.8 ng of added vanadium plus the 0.8 ng of vanadium from the water blank suggests a practical sensitivity limit of 2 ng. Good linearity is illustrated by the photopeak counts given in Table 1 for the range of vanadium concentrations considered.

Table 1. Recovery of vanadium from water.

Vanadium added (ng)	Percent recovery	Vanadium photopeak counts (counts/2 min.)
80	104	6207
40	99	2955
16	103	1276
8	100	651
3.2	97	292
0.8	125	130[a]
Water blank	---	60[b]

---

[a] Corrected for ^{28}Al Compton contribution to the 1.43 MeV photopeak of ^{52}V.

[b] The vanadium "background" was approximately 0.8 ng.

In Figure 1, the ^{52}V photopeak is well defined at both 80 and 8 ng of added vanadium with good counting statistics realized in each case. The ^{28}Al photopeak in Figure 1 for 8 ng of added vanadium is barely visible, at 1.78 MeV but ^{28}Al is a significant part of the spectrum in Figure 2 for 0.8 ng of added vanadium. The ^{38}Cl in the casein base diet (Fig. 2) is a significant part of the spectrum. Both ^{28}Al and ^{38}Cl, having gamma-ray energies greater than 1.43 MeV contribute counts to the vanadium photopeak, and corrections can be readily made. However, some samples can be dominated by these interferences causing poorer sensitivities. In such cases further modification of the procedure such as a

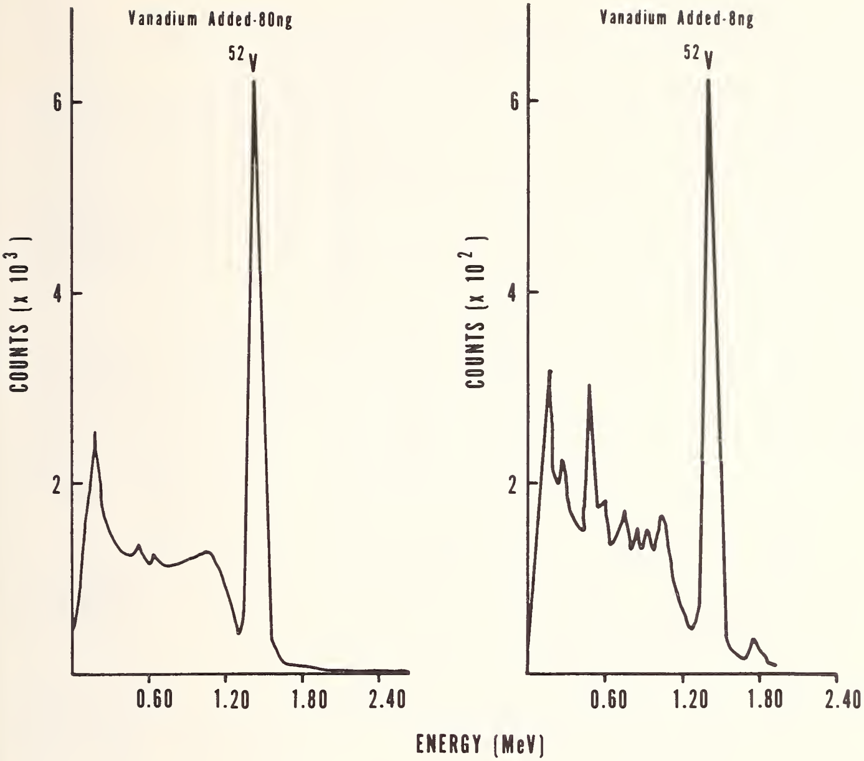

Figure 1. Gamma-ray spectra of ^{52}V recoveries.

change in the extracting solvent to remove the interferences may be required.

When chromium and manganese are present in a sample matrix the competing reactions ^{52}Cr(n,p)^{52}V and ^{55}Mn(n,α)^{52}V due to fast neutrons can interfere. However, the quantity of these elements in most foods and biological samples is sufficiently small that errors due to these interferences are insignificant. For example, the interferences due to chromium and manganese in the Casein Diet of Figure 2 which contained only 14 parts per billion (ppb) vanadium was estimated to be equivalent to less than 1 ppb vanadium.

Generally, the sensitivity of the method is a factor of the separation time, the chemical procedure, and the sample matrix. Nanogram sensitivities are feasible with a precision of approximately 30% at a 95% confidence level.

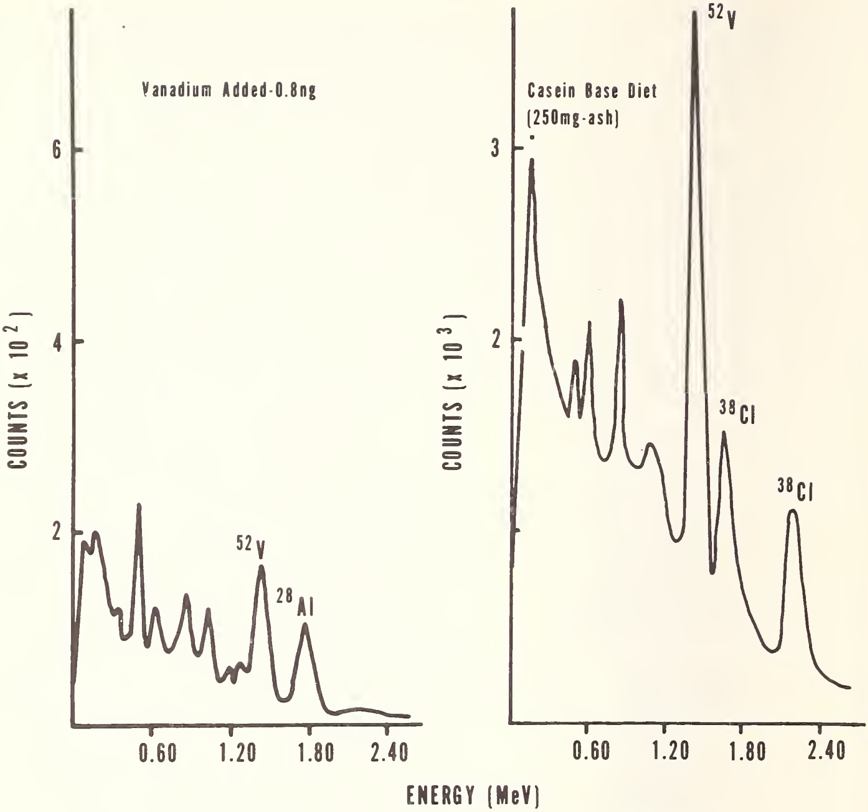

Figure 2. Gamma-ray spectra of ^{52}V spectral interferences.

B. Vanadium-free Diet

Diets for experimental animals and several dietary constituents were analyzed for vanadium using the described procedure. The results are given in Table 2. An ordinary commercial chow, analyzed for comparison, contained four times as much vanadium as a laboratory prepared Torula Diet. The Torula Diet contains 40% Torula yeast and 6% commercial Fox Briggs N Salt Mix. These constituents had the highest vanadium content of those listed in Table 2, and contributed nearly 85% of the vanadium to the laboratory prepared Torula Diet. The contribution to the diet of the three other constituents is relatively minor compared to that of these major sources of vanadium.

With the use of reagent grade salts a laboratory salt mix was prepared [3] which contained only 65 ppb vanadium. Of the protein base materials

Table 2. Vanadium determined in experimental diets and dietary constituents.

Sample description	Source	Vanadium content (ppb)
	Available Diets	
Commercial diet	Purina Laboratory Chow	885
Torula diet	FDA Laboratory	210
	Major Diet Constituents	
Fox-Briggs N salt mix	General Biochemicals	2000
Torula yeast NF × 11	St. Regis, Rinelander, Wis.	140
Vitamin mixture	Nutritional Biochemicals	15
Sucrose	Domino Pure Cane Sugar	10
Stripped lard	Distillation Product Industries	2
	Possible Substitutes for Diet Constituents	
Fox-Briggs N salt mix	FDA Laboratory	65
Casein	General Biochemicals	15
	"Vanadium Free" Diet	
Casein diet	FDA Laboratory	14

casein was lower in vanadium than Torula yeast by almost a factor of ten. The laboratory prepared Casein Diet consisted of 67% sucrose, 20% casein, 6% laboratory salt mix, 5% stripped lard, and 2% vitamin mixture. When compared with other available diets, this diet was considered to be vanadium-free at only 14 ppb.

The developed analytical method was sensitive enough to be used effectively in determining the vanadium levels in a large variety of food samples.

IV. Acknowledgment

The authors wish to thank the Reactor Branch personnel at the Naval Research Laboratory for their assistance throughout the program.

The dietary preparations and animal feeding studies described in this paper are being conducted by Dr. L. L. Hopkins and Mr. H. E. Mohr of the Division of Nutrition, Bureau of Science, Food and Drug Administration.

V. References

[1] Schroeder, H. A., Balassa, J. J., and Tipton, I. H., "Abnormal Trace Metals in Man-Vanadium" in J. Chron. Dis. **16,** 1047-1071 (1963).

[2] Wahl, W. H., Molinski, V. J., and Arino, H., "Rapid Radiochemical Separation Procedures for Activation Analysis Indicator", in Proceedings – Modern Trends in Activation Analysis, College Station, Texas (1965), pp. 44-47.

[3] Fox, M. R. S., and Briggs, G. M., "Fox-Brigg N Salt Mix", Journal of Nutrition **72,** 243 (1960).

THE INSTRUMENTAL DETERMINATION OF FIFTEEN ELEMENTS IN PLANT TISSUE BY NEUTRON ACTIVATION ANALYSIS

William A. Haller and Royston Filby

Washington State University
Department of Chemistry
Pullman, Washington

Louis A. Rancitelli and John A. Cooper

Battelle Memorial Institute
Pacific Northwest Laboratory
Richland, Washington

I. Introduction

Many studies have been performed to determine the effect of trace element concentrations on plant growth [1,2], however, at present the trace elements essential to plant growth have been only partially defined [3]. A major limitation to extensive trace element studies in plant samples had been the lack of practical methods for the measurement of a large group of trace elements in the part per million (ppm) to part per billion (ppb) range. Methods of analysis vary from wet chemical techniques to spectrographic and flame photometric procedures.

In the last decade, neutron activation analysis has become an increasingly useful tool for trace elemental analysis. For many elements, activation analysis is the most sensitive technique known. Another advantage of activation analysis is that reagent contamination of the sample can be avoided where no preirradiation chemical treatment is conducted. With the advent of the Ge(Li) crystals it has recently been shown [4] that the selectivity for activation analysis of biological tissue can be greatly extended. The purpose of the study that was undertaken was to develop a scheme for multielement analysis of plant tissue by neutron activation and Ge(Li) analysis which was reasonably simple and essentially contamination free.

II. Experimental

A. Sample Preparation

The main emphasis of the study was in establishing method feasibility rather than relating trace element concentrations to environmental or biological parameters. Several special techniques were employed in sample handling and encapsulation prior to irradiation. Preirradiation sample preparation was performed in a clean hood. High moisture samples were sectioned with a lucite borer and placed in a polyethylene container (Nalgene Number 25) which had been leached with double distilled H_2O and HNO_3. Grain samples were placed directly in the containers. The samples were dehydrated by drying them for two days in a Thermovac Freeze Unit. After freeze drying the polyethylene containers were taped shut with plastic tape and wrapped in several layers of 0.003 cm aluminum foil.

B. STANDARDS

The high resolution of the spectrometer allowed the use of mixed standard solutions. Because of chemical incompatibility of some elements, three standard solutions were used.

C. NEUTRON IRRADIATION AND POST IRRADIATION TREATMENT

The samples were irradiated to an integrated neutron exposure of 7×10^{17} n/cm^2 in a graphite moderated reactor. Several samples were irradiated in a TRIGA-III type reactor at a flux of approximately 1×10^{13} $n \cdot cm^{-2} \cdot sec^{-1}$, integrated exposure 5×10^{17} n/cm^2.

After irradiation the samples were allowed to decay for 12 hours and transferred to a one inch dish for gamma-ray analysis.

D. SOLID STATE GE(LI) SPECTROMETER

The solid state Ge(Li) spectrometer used was a 20 cubic centimeter coaxial drifted diode with a system resolution, measured at the ^{60}Co 1.33 MeV line, of 3.4 keV and a peak to Compton ratio of 12 to 1.

For several samples a newer Ge(Li) crystal with a system resolution, measured at the ^{60}Co 1.33 MeV line, of 3.0 keV and a peak to Compton of 14 to 1 was used.

E. DATA ACQUISITION

After a 12 hour decay period, a 20 minute count on the Ge(Li) spectrometer was taken to measure the short-lived activation products ^{24}Na, ^{42}K, ^{56}Mn and ^{64}Cu. Following a decay period of approximately 48 hours, the samples were recounted to measure the ^{76}As and ^{82}Br. The samples were then allowed to decay an additional eight weeks to permit these short-lived radionuclides to decay. During this decay period the troublesome bremsstrahlung radiation, which is mainly due to ^{32}P energetic beta particles, is reduced by about 16 fold. The samples were then counted for periods of 1000 minutes to measure the long-lived activation products ^{32}P, ^{51}Cr, ^{59}Fe, ^{60}Co, ^{65}Zn, ^{75}Se, ^{86}Rb, ^{134}Cs and ^{203}Hg. The neutron activated standards were counted at appropriate times and compared directly with the samples. Figure 1 shows a gamma spectrum of samples recorded at various times after irradiation. Table 1 shows the decay characteristics of the neutron induced radionuclides.

II. Results

Table 2 shows the elemental concentrations observed in the various samples which were studied. Standard deviations were calculated in the usual manner [5]. Comparison of replicate samples showed the average deviation about the mean to be less than 10% for Se, Fe, Zn, Mn, and Cu and less than 25% for the remainder of the elements. In the case of Co, Cs, Cr, P and Hg, the calculated standard deviations based on counting

Table 1. Decay characteristics of the daughter radionuclides produced by neutron irradiation of plant tissue.

Parent element	Daughter radionuclide	Half life	Gamma ray measured (MeV)	Other prominate gamma rays (MeV)
Manganese	^{56}Mn	2.6 h	.845	1.81
Potassium	^{42}K	12.5 h	1.523	---
Copper	^{64}Cu	12.8 h	.511	---
Sodium	^{24}Na	15.0 h	1.367	2.752
Arsenic	^{76}As	26.3 h	.559	---
Bromine	^{82}Br	35.8 h	.777	.554, .618, 1.317
Phosphorus	^{32}P	14.3 d	bremsstrahlung	---
Rubidium	^{86}Rb	18.6 d	1.079	---
Chromium	^{51}Cr	27.8 d	.320	---
Iron	^{59}Fe	45.1 d	1.095	1.292
Mercury	^{203}Hg	46.9 d	.279	---
Selenium	^{75}Se	120.4 d	.264	.279, .139
Zinc	^{65}Zn	245 d	1.115	.511
Cesium	^{134}Cs	2.05 y	.797	.605
Cobalt	^{60}Co	5.2 y	1.172	1.332

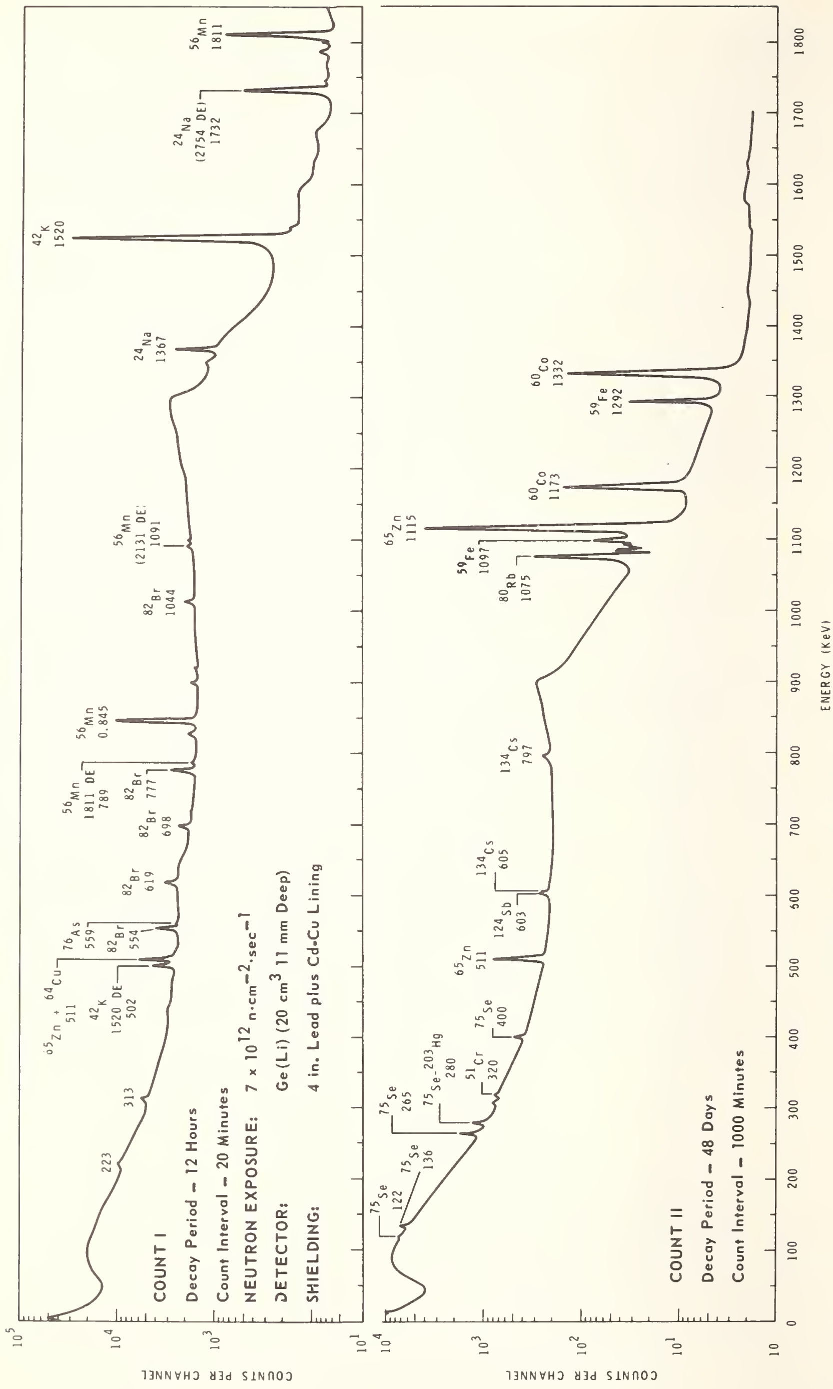

Figure 1. Gamma spectra of neutron activated lima bean.

statistics account for the observed variations. The relatively high deviations of Br, Rb, Na, and K cannot be accounted for by statistical considerations. Since these elements are usually in a highly mobile form, slight variation in growing conditions and/or processing could possibly account for these differences. The elemental concentrations observed in this study were in the same range as published compilations [6,7].

Rather large statistical variations occur with some of the Co, Cs, Se and Hg concentrations. In the case of Co and Cs the high variations are due to the lack of a sufficient number of counts from the neutron activated daughter products. The Cr, Se and Hg high statistical deviation is also related to the low count rate, but of more importance are the large Compton correction associated with the higher energy gamma rays and bremsstrahlung from ^{32}P. Since these measurements were made with a 1000 minute count, it would seem unrealistic to attempt to improve the statistics by a longer counting period. However, as can be seen from Table 2, the sample weights are approximately .4 to 2 grams. At present the irradiation system at the TRIGA III reactor is being modified to hold samples weighing at least 10 grams. This sample weight increase should considerably improve the problem of low count rate and/or reduce the counting time of the samples. An important feature of this analytical method is that a large number of what are now considered to be essential trace elements can be measured simultaneously. Such measurements

Table 2. Elemental concentration in plant tissue.

Element	Rice[a,b]	Rice[a,b]	Rice[a,b]	Barley[a,c]	Barley[a,c]	Barley[a,c]
Wet weight grams	.438	.490	.442	.527	.469	.408
			Nanogram/gram			
Cobalt	27 ± 2	20 ± 2	18 ± 2	3 ± .5	2 ± .5	1.2± .5
Cesium	4 ± 1	4 ± 1	3 ± 1	<1	<1	<1
Chromium	35 ±10	33 ±10	27 ±10	19 ± 12	16 ± 11	30 ± 13
Selenium	113 ± 7	115 ± 7	90 ± 6	50 ± 2	64 ± 3	58 ± 3
Mercury	62 ±15	59 ±15	66 ±15	117 ± 30	58 ± 26	90 ± 30
Arsenic	<100	<100	<100	<100	<100	<100
			Microgram/gram			
Iron	4.7± .7	4.2± .6	4.2± .6	11.2± 1	12.3± 1	11.9± 1
Rubidium	3.1± 2	2.9± .2	2.0± .2	.8± .1	.8± .1	.9± .1
Zinc	18.3± .2	19.7± .2	18.1± .2	14.6± .7	14.9± .8	15.1± .8
Manganese	23.8± .2	22.9± .2	23.2± .2	16.8± .1	16.2± .1	17.0± .1
Sodium	29.1± .4	29.6± .3	26.9± .3	40 ± 2	58 ± 3	39 ± 2
Potassium	1460 ±20	1681 ±18	1699 ± 8	1865 ± 10	2211 ± 11	2008 ± 12
Copper	.7± .1	.8± .1	.8± .1	2.8± .2	3.0± .2	2.4± .2
Bromine	7.1± 1	5.9± .2	6.0± .2	4.4± .3	6.0± .4	4.8± .2
Phosphorus	345 ±50	215 ±42	400 ±56	2400 ±300	2375 ±290	2164 ±285

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[a] Replicate samples taken from same container.

[b] Rice, Blue Rose, Centennial brand.

[c] Barley, Pearl Barley, Centennial brand.

Table 2. Elemental concentration in plant tissue. (continued)

Element	Raisin[d]	Lima bean[e]	Pea[f]	Apple[g]	Pear[h]
Wet weight grams	.576	1.365	.463	1.606	3.317
			Nanogram/gram		
Cobalt	10 ± .5	58 ± 2	128 ±	21.9 ± .3	10 ± .2
Cesium	54 ± 2	18 ± 1	<1	<1	<1
Chromium	75 ± 11	27 ± 10	34 ± 11	37 ± 1	29 ± 1
Selenium	<1	61 ± 4	<1	22 ± 7	21 ± 7
Mercury	63 ± 18	36 ± 16	25 ± 15	20 ± 3	13 ± 3
Arsenic	<100	<100	<100	18 ± 6	46 ± 6
			Microgram/gram		
Iron	27.5± 1	34.2± 1	33.5± 1	2.1 ± .3	1.6 ± .2
Rubidium	15.6± .2	19.9± .8	0.5± .1	0.9 ± .1	0.5 ± <.1
Zinc	1.5± .2	23 ± .5	22 ± .6	24 ± .4	1.4 ± .2
Manganese	4.2± .1	11.5± 4	23.3± .2	0.3 ± .07	0.8 ± .04
Sodium	118 ± 1	78 ± 2	78 ± 2	14 ± 1.1	7.6 ± .4
Potassium	7200 ± 10	11490 ±441	7637 ± 70	1187 ± 5	1064 ± 2
Copper	1 ± .4	4.9± .2	5.3± .1	0.3 ± .05	0.7 ± .1
Bromine	8.1± .2	2.4± .2	18.3± .7	<.05	<.05
Phosphorus	1699 ±210	4081 ±365	4110 ±210	180 ±15	130 ±15

[d] Raisins, SunMaid.

[e] Lima Beans, dried, Centennial brand.

[f] Pea, dried and split.

[g] Apple, Fresh less skin and core.

[h] Pear, Fresh less skin and core.

should help to establish the physiological significance of these elements and other trace elements such as Cr, Se, Hg, As, and Rb in the life processes.

The actual working time involved in sample preparation and analysis is relatively small since it involves only freeze drying, irradiation and counting of the sample. The mathematical reduction of the count rate from the spectrum can be handled manually in about one hour for the 15 elements. Because a large group of trace elements can be measured simultaneously, the direct applicability of this method to all manner of plant samples appears certain and is already proving extremely useful.

IV. References

[1] Kuhn, H., and Schaumloffel, E., Effects of High Copper Rates on Cereal, Landwintsch Torsch. **14**, 82-90 (1961).

[2] Monier, S., and Williams, L., "Trace Elements in Food", John Wiley and Sons, Inc., New York.

[3] Lamb, C. A., Bentley, J. M., Trace Elements Conference at the Ohio Agriculture Station, Wooster, Ohio, (1957), pp. 1-10.

[4] Perkins, R. W., Haller, W. A., and Thorpe, J. D., Trace Element Analysis of Human Lung Tissue by Neutron Activation and Instrumental Analysis BNWL-SA-992, Presented at the IAEA Symposium on Nuclear Activation Techniques in the Life Sciences, the Amsterdam, The Netherlands, May 8-13, 1967.

[5] Friedlander, G., Kennedy, J. W., and Miller, J., "Nuclear and Radiochemistry", 2nd ed., Wiley, New York, 1964, pp. 166-189.

[6] Mattice, M., "Bridges Food and Beverage Analysis", 3rd ed., Lea and Tibiger (1950).

[7] Wooster, H. A., Black, F. C., "Nutritional Data", H. J. Heinz Co., Pittsburgh, Pa. (1955).

SIMULTANEOUS DETERMINATION OF ARSENIC, ANTIMONY AND MERCURY IN BIOLOGICAL MATERIALS BY NEUTRON ACTIVATION ANALYSIS

I. Hadzistelios and A. P. Grimanis

Chemistry Division
Nuclear Research Center "Democritos"
Athens, Greece

I. Introduction

There is an expanded interest for the determination of toxic elements such as arsenic, antimony and mercury in several materials. Many workers have determined these elements in biological materials by combined chemical separation and neutron activation analysis methods [1-7]. It seems however that arsenic, antimony and mercury have been determined simultaneously only by Samsahl [8] in biological materials and by Kiesel [9] in meteorites.

The present paper based on previously reported extraction studies [10] describes a simple and rapid neutron activation analysis method for the simultaneous determination of arsenic, antimony and mercury in biological materials.

II. Experimental

A. Apparatus and Reagents

A NaI(Tl) crystal 3 in. × 3 in. coupled with an Intertechnique 400 channel pulse-height analyzer with a NaI(Tl) well-type scintillation crystal (2 in. × 1.75 in.) connected with a single channel analyzer were used. The stock of the resin Dowex 1X8, 100-200 mesh, (Cl^-) form was treated before use with water, 8 M, 4 M, 1 M hydrochloric acid solutions and finally with water. The resin column was 11 mm × 100 mm and equilibrated with 4 M HCl before use. Analytical reagent grade materials were used. Aqueous solutions of carriers were prepared to contain 20 mg arsenic (arsenic pentoxide) per ml, 10 mg antimony (tartar emetic) per ml and 10 mg mercury (mercuric acetate) per ml. A mixed standard of arsenic and mercury solution was prepared to contain 0.5 μg arsenic per ml and 1 μg mercury per ml. The antimony standard solution contained 1 μg antimony (antimony metal) per ml of 9 M sulfuric acid solution. The standards for the reactivation procedure were prepared to contain 80 μg arsenic per ml, 80 μg antimony per ml and 200 μg mercury per ml. A stock solution of arsenic (solution A) containing 35 mg arsenic per ml of 10 M sulfuric acid solution was made. A rinsing mixture of 10 *M* sulfuric acid 0.05 *M* hydrobromic acid was also prepared.

B. PROCEDURE

Biological materials (150-250 mg) were placed in quartz tubes (9 mm × 50 mm). Aliquots (0.5 ml) of the mixed standard arsenic and mercury solution and of the standard antimony solution were placed in identical quartz tubes. Precautions were taken during the quick heat-sealing of tubes by covering them with a strip of ice-cold wet asbestos. Tubes were placed in the rotating system of the reactor and irradiated for 20 hours in a thermal neturon flux of about 1.5×10^{12} n·cm^{-2}·sec^{-1}. After irradiation and a cooling time of 12 hours each quartz tube was immersed in aqua regia, rinsed with water and then placed into a polyethylene vial (18 mm × 60 mm) containing 3 ml concentrated nitric acid. The quartz tube was crushed and the contents ot the vial were transferred into a 150 ml wide-necked Erlenmeyer flask according to the procedure given by Sjostrand [3]. Twenty mg of each of the arsenic, antimony and mercury carriers and 4.5 ml 18 *M* sulphuric acid were added into the flask. Digestion of the sample was made by heating twice with 4 ml of fuming nitric acid until white fumes of sulfuric acid were evolved. The resulting solution was made 10 *M* in sulfuric acid −0.5 *M* in hydrobromic acid (with cooling) and transferred into a separatory funnel containing an equal volume of benzene (15 ml). Arsenic and antimony were extracted into the organic phase by shaking for 2 min. The aqueous phase was drawn off to another funnel for the mercury separation. The organic phase was washed twice with the rinsing solution and washings were discarded. The arsenic and antimony were stripped from benzene by shaking with 5 ml 4 *M* hydrochloric acid, and the acid solution transferred onto the resin column No. 1. To the funnel containing the mercury, 5 ml of "solution A" were added and the mercury extracted by shaking with 20 ml of benzene for 2 min. The aqueous phase was shaken again with 10 ml of benzene, and the mercury was stripped from the combined organic phases with 5 ml of 4 *N* hydrochloric acid. This acid solution was transferred onto a resin column No. II similar to the previous No. I used for the fixation of arsenic and antimony. Arsenic and antimony were eluted from column No. I with 45 ml 4 *M* HCl and 40 ml 2.7 *M* ammonium fluoride-0.4 *M* hydrochloric acid, respectively, and effluents collected in centrifuge tubes. The column No. II was purified from arsenic and antimony activities as before and mercury eluted with 45 ml 0.15 *M* thiocarbamide-0.01 *M* hydrochloric acid. The effluent was collected in a 50 ml volumetric flask and diluted to volume with water. The mercury-standard was analyzed in the same manner. The ^{197,197m}Hg gamma-ray activity of sample and standard in the volumetric flasks was measured on the multichannel analyzer.

Arsenic and antimony were precipitated with sodium hypophosphite and thioacetamide, respectively. The precipitates were redissolved; arsenic in nitric acid and antimony sulfide in concentrated hydrochloric acid. Solutions were transferred into 5 ml volumetric flasks. Arsenic and antimony solutions were diluted to volume with water and 6 *M* hydrochloric acid, respectively. The arsenic and antimony standards were analyzed by an identical manner. The ^{76}As and ^{122}Sb gamma-ray activities of sample and standard in the volumetric flasks were measured on the well-type counter.

After counting, the chemical yield of the isolated elements was determined by a reactivation technique. Aliquots of samples and standards were pipetted from the volumetric flasks containing arsenic, antimony and mercury and diluted to a known volume. One ml aliquots of these diluted solutions and of the reactivation standards were transferred into polyethylene vials which were irradiated for 15 min. After a 24 hour cooling time the vials were counted on a multichannel analyzer. The chemical yield was found by comparing the corresponding photopeak areas of ^{76}As, ^{122}Sb and ^{197,197m}Hg of samples and reactivation standards.

III. Results and Discussion

A. RESULTS

Results of the determination of arsenic, antimony and mercury in biological samples are shown in Table 1. The values of these elements found in the biological standard (kale sample) were in good agreement with those found by other laboratories for the same sample [11]. The reproducibility of the method is shown in Table 2 where results of the analyses of 4 kale samples are tabulated. The chemical yield of the isolated elements is also listed.

Table 1. Arsenic, antimony and mercury content of biological materials.[a]

Biological sample	Arsenic ng/g	Antimony ng/g	Mercury ng/g
Kale	136	73	183
Animal blood	20	54	108
Pine leaves	369	224	60

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[a] Results are means of at least duplicate analyses and referred to dried samples.

Table 2. Arsenic, antimony and mercury determination in four identical samples of standard kale.

	Arsenic		Antimony		Mercury	
Sample No.	ng/g	chemical yield (%)	ng/g	chemical yield (%)	ng/g	chemical yield (%)
1	161	79.2	92	96.0	197	56.3
2	122	80.7	94	83.3	169	67.0
3	123	80.8	52	95.1	168	60.8
4	137	76.5	54	91.4	200	65.8

B. Discussion

The separation scheme of the elements outlined in the proposed method is shown in Figure 1. Digestion of the sample with nitric and sulfuric acid was made in an open system because in absence of chloride ions a recovery greater than 98% for arsenic and antimony and about 95% for mercury was found. However, even in the presence of 100 mg chloride the recovery of mercury is greater than 70%. For the isolation of arsenic, antimony and mercury, a combined solvent extraction-ion exchange procedure was followed. The advantages of the extraction step are simplicity and rapidity. The general features of the extraction were based on our previously reported work [10]. The only modification made was to vary the molarity of hydrobromic acid which affects the extractability of mercury. Extraction was made in 2 steps. In the first step arsenic and antimony were extracted almost quantitatively into benzene from a 10 *M* sulfuric acid—0.5 *M* hydrobromic acid and isolated from many other radionuclides. Less than 7% mercury is extracted into benzene. In the second step mercury is extracted twice into benzene in greater than 90% amounts and separated from the radioactivity of other radioisotopes. This was accomplished by reducing the concentration of bromide ions in the aqueous phase adding arsenic which forms arsenic tribromide which is extracted into benzene.

The elements arsenic and antimony with mercury impurity isolated after the first extraction step, were separated from each other by an anion chromatographic elution procedure (Fig. 2). The same elution procedure was followed to isolate mercury from arsenic, antimony and other impurities present in the solution resulting from the second extraction step (Fig. 2).

Decontamination factors of ^{76}As, ^{122}Sb and ^{197,197m}Hg separated on the resin from each other were of the order of 10^5, taking the extraction steps

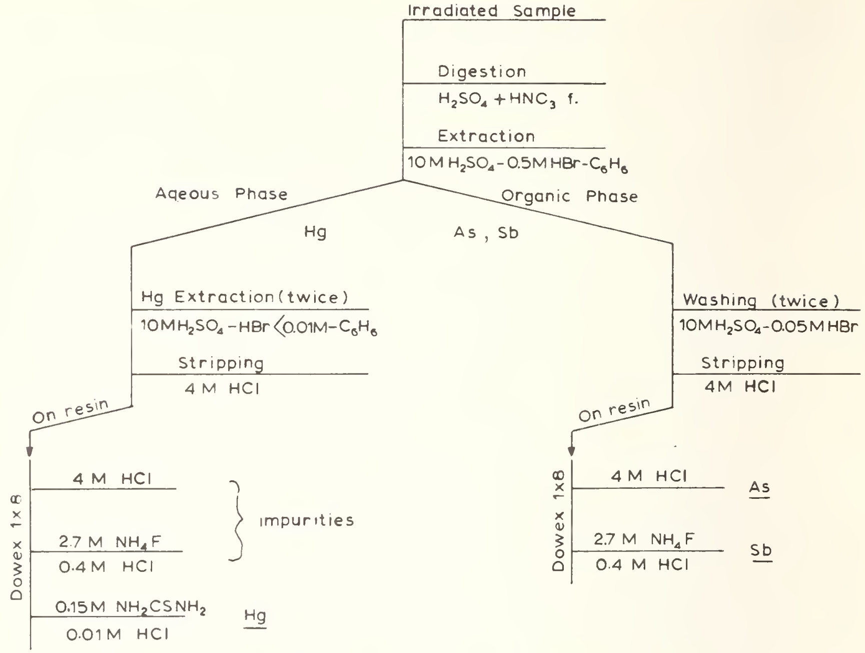

Figure 1. Separation schemes for arsenic, antimony, and mercury.

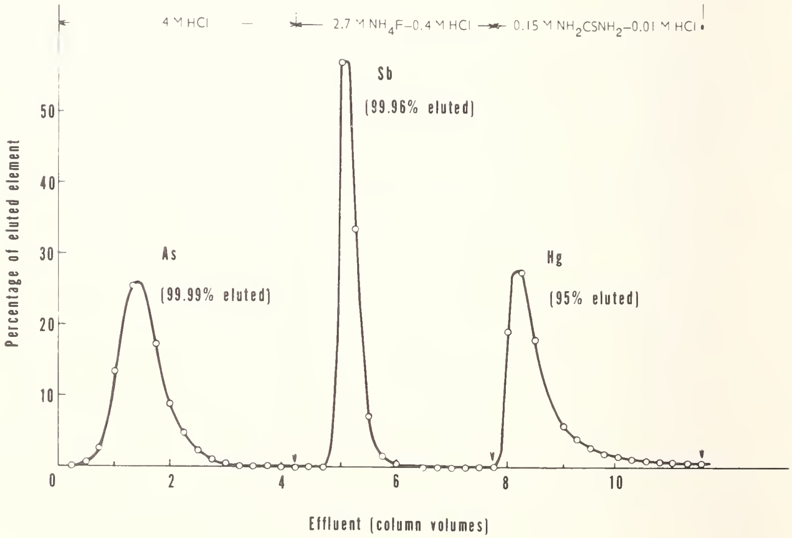

Figure 2. Chromatographic separation of arsenic, antimony, and mercury on column Dowex 1×8 100-200 mesh 1.1 cm^2×10 cm; 11 cm^3, flow rate = 1.5 to 2 ml · cm^{-2} · sec^{-1}.

into consideration. Final decontamination factors of the order of 10^6 for barium, bromine, cadmium, chlorine, copper, gallium, indium, manganese, potassium, sodium, scandium, strontium and zinc were found for all three separated elements. Gold is extracted less than 0.5% into benzene during mercury extraction, but follows mercury on the resin procedure. The precipitation of arsenic was made in order to eliminate the interference of germanium which was also extracted into benzene and eluted from the column. Selenium also follows arsenic in the final step of separation, but if present it can be eliminated by selective reduction. The precipitation of antimony was done only to reduce volume and improve sensitivity. The time required for the radiochemical separation of the 3 elements in 6 samples is 3 1/2 hours. The sensitivities found were 0.005 μg for arsenic, 0.010 μg for antimony and 0.020 μg for mercury.

The proposed neutron activation analysis method for the simultaneous determination of arsenic, antimony and mercury in biological materials is sufficiently rapid, simple and convenient for a series of analyses.

V. References

[1] Bowen, H.J.M., and Gibbons, D., Radioactivation Analysis, Clarendon Press, Oxford, 1963.
[2] Lyon, W. S., Guide to Activation Analysis Appendix A, Van Nostrand, New York 1964.
[3] Sjostrand, B., Anal. Chem. **36**, 815 (1964).
[4] Kim, C. K., and Silverman, J., Anal. Chem. **37**, 1617 (1965).
[5] Livingston, H. D., Smith, H., and Stojanovic, N., Talanta **14**, 505 (1967).
[6] Bowen, H.J.M., Analyst **92**, 118 (1967).
[7] Van den Winkel, P., Speecke, A., and Hoste, J. J., IAEA Symposium on Nuclear Activation Techniques in the Life Sciences, Amsterdam, Netherlands, May 8-12, 1967, Paper No. SM-91/30, p. 159.
[8] Samsahl, K., Anal. Chem. **39**, 1480 (1967).
[9] Kiesel, W., Z. Anal. Chem. **227**, 13 (1967).
[10] Grimanis, A. P., Hadzistelios, I., Anal. Chim. Acta **41**, 16 (1968).
[11] Bowen, H.J.M., Analyst **92**, 124 (1967).

INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS OF TOBACCO PRODUCTS

R. A. Nadkarni and W. D. Ehmann

Department of Chemistry
University of Kentucky
Lexington, Kentucky 40506

I. Introduction

Tobacco is one of the plants most often used in the study of mineral nutrition. Current interest in the production of tobacco and the physiological effects of human consumption of tobacco, make it desirable to study the inorganic microelements in tobacco products. Research up to 1964 has been admirably summarized by Tso [1]. His paper points out the sketchy nature of the knowledge of mineral concentrations in tobacco leaf and their transference into smoke. In view of the number of elements of suspected toxicity present in tobacco this study is of singular interest. The techniques used in this study may also be applied to trace element analyses in a wide variety of biological matrices.

The sensitive technique of activation analysis is well suited for this study in view of the trace concentrations of these elements. In this study instrumental neutron activation analysis (INAA) utilizing a high resolution Ge(Li) detector has been employed. This detector permits resolution and characterization of close lying gamma-ray energies. The work presented here is confined to the abundances of 11 elements in tobacco. The studies on the transferrence of these elements into smoke and residual ashes will be reported at a later date.

II. Experimental

A. Sample and Standard Preparation

The tobacco leaves were collected from the burley tobacco plants grown in the vicinity of Lexington, Kentucky. The cigarette, cigar or pipe tobacco samples were taken from commercial cigarette and tobacco packets. Except for drying the samples at 90 °C for 12 hours no pretreatment was carried out on these samples. The standards were prepared by spiking "Specpure" silicon dioxide with known weights of dilute standard solutions. Samples and standards were sealed in small high purity quartz ampoules.

B. IRRADIATION

Irradiation units usually consisted of ten tobacco samples weighing between 5 and 30 mg and six standards containing about 1 to 10 μg of the elements to be determined. The units were irradiated at a thermal neutron flux of approximately 1×10^{13} n·cm^{-2}·sec^{-1} for a period of 6 to 7 days in either the Argonne CP-5 or Air Force NETF reactor, Dayton, Ohio.

After irradiation the exteriors of the quartz ampoules were cleaned in hot aqua regia. The samples were not removed from the ampoules to prevent possible escape of volatile elements such as bromine, selenium, and arsenic. Blank ampoules containing only "Specpure" SiO_2 were also irradiated, cleaned and counted under identical conditions. These showed no interfering gamma rays for the 11 elements under study.

C. COUNTING TECHNIQUE

The activities of the samples were measured with a 400 channel pulse height analyzer coupled to a Ge(Li) coaxial detector of 12 ml active volume and a full width at half maximum of about 4.7 keV for the 1.33 MeV photopeak of ^{60}Co. A pulse stretcher and a biased amplifier were used to expand regions of interest in the gamma-ray spectrum. Because of the low efficiency of the detector, measurements were taken without external shielding. The 1.46 MeV gamma ray of ^{40}K from the background is observed in the spectra on counting for long periods.

Characterization of the observed gamma rays was based mainly on the energies of the lines. Due to the high resolution of the detector the energies of these lines can easily be determined to within ±2 keV. For short-lived species like ^{82}Br and ^{140}La, half lives were also determined. The system was calibrated with several standard sources every time a set of readings was taken. The pulse height *vs.* energy curve was found to be consistently linear in the energy region of interest.

The areas under the photopeaks were integrated and a baseline subtracted based on interpolation of points on both sides of the peak. Necessary corrections for decay times and counting times have been applied.

In the thermal neutron activation of tobacco, the main activities produced are due to ^{24}Na and ^{42}K. However, these being short-lived species (half lives of 15.5 h and 12.4 h, respectively) they decay quickly and it is possible to observe the well-defined photopeaks of ^{140}La, ^{82}Br and ^{76}As within one week after the irradiation. These and other short-lived activities decay to insignificant levels after a period of 30-45 days and most of the long-lived nuclides may be measured at this stage. Table 1 lists the energies of the gamma rays of radionuclides used in these determinations. Zinc values have been corrected for the contribution from the 1.121 MeV peak of ^{46}Sc to the 1.119 MeV peak of ^{65}Zn.

Table 1. Energies of the gamma rays of indicator radionuclides.

Element	Indicator radionuclide	Half life	γ–ray used in the determination[a] (MeV)
Lanthanum	^{140}La	40.22 h	0.487
Bromine	^{82}Br	35.3 h	0.777 (0.619, 0.698)
Arsenic	^{76}As	26.4 h	0.648
Chromium	^{51}Cr	27.8 d	0.32
Selenium	^{75}Se	120 d	0.401
Silver	^{110m}Ag	253 d	0.658
Zirconium	^{95}Zr	65 d	0.757
Scandium	^{46}Sc	83.9 d	0.89
Antimony	^{124}Sb	60 d	0.603 (1.691)
Zinc	^{65}Zn	245 d	1.119 (0.51)
Cobalt	^{60}Co	5.27 y	1.33 (1.17)

[a] Other γ–rays that could be used for determinations are given in parenthesis.

III. Results and Discussion

Figures 1 and 2 show the spectra of irradiated burley tobacco leaf and commercial tobacco, respectively.

Tables 2 to 4 give the results of determination of La, Br, As, Cr, Ag, Se, Zr, Sc, Sb, Zn, and Co in burley tobacco leaves, stalks, ashes and 19 different brands of commercial cigarette tobacco and two brands each of pipe and cigar tobacco, as well as cigarette papers used with 12 different brands.

La, Sb and Zn have a lower abundance in tobacco stalks than in tobacco leaves. The reverse is true for Br and Se. In all cases except Sb and Co the concentrations of elements are about the same in tobacco leaves and cigarette fillers. Values for Sb are higher and for Co lower in cigarette fillers than in tobacco leaves. La and Zn are higher and Sc is lower in pipe and cigar tobacco, but levels of other elements seem to be about the same as in cigarette tobacco. In cigarette paper the amounts of Br, Sc and Co are lower than in tobacco; the amount of Zn is approximately the same, while Se seems to be slightly higher than in tobacco. Concentrations of lanthanum and antimony seem to divide the papers into two classes— one having La between 0.27-1 parts per million

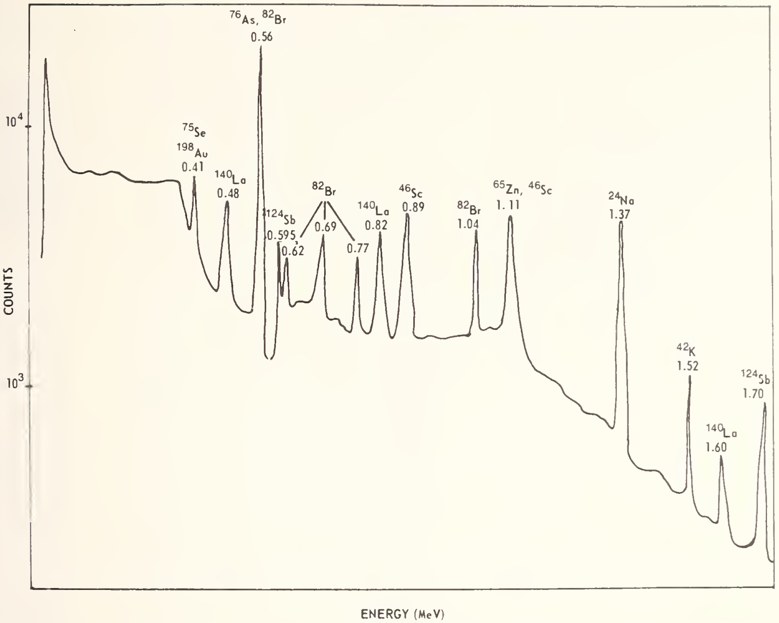

Figure 1. Burley tobacco leaves irradiated for 7 days and counted for 10 minutes after a decay of 3 days.

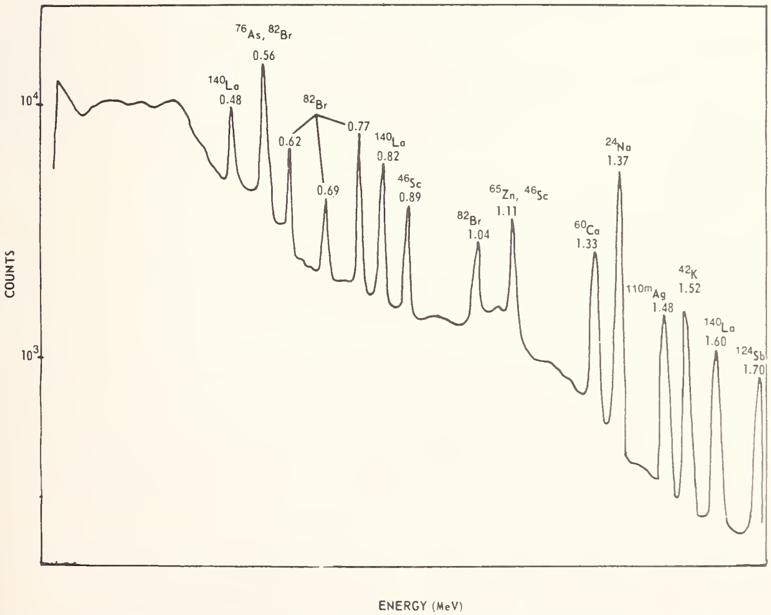

Figure 2. Commercial cigarette tobacco irradiated for 7 days and counted for 10 minutes after a decay of 3 days.

Table 2. Determination of lanthanum, bromine, and arsenic in tobacco products by INAA.

Material analyzed	Lanthanum (ppm)	Bromine (ppm)	Arsenic (ppm)
Burley tobacco leaves	0.36 (2)[a]	58 (2)	2.5 (5)
Burley tobacco ashes	1.50 (3)	7.6 (2)	
Burley tobacco stalks	0.04–0.2	78	
Cigarette tobacco			
Brand A	0.45	154	4.5 (2)
B	0.64	78	3.3 (2)
C	0.51 (2)	36 (2)	7.3 (2)
D	0.41 (2)	61 (2)	15.4 (2)
E	0.23 (2)	114 (2)	4.5 (2)
F	0.27 (2)	97 (2)	1.79 (2)
G	0.53 (2)	65	10.2 (2)
H	0.25 (2)	76 (2)	6.1 (2)
I	0.33 (2)	58 (2)	5.2 (2)
J	0.82 (2)	56 (2)	9.6 (2)
K	0.22 (2)	48 (2)	10.7 (2)
L	0.36 (2)	140 (2)	3.7 (2)
M	0.32 (2)	68 (2)	2.9–12
N	0.38 (2)	59 (2)	57 (2)
O	0.20 (2)	148 (2)	2.6 (2)
P	0.14 (2)	80 (2)	3.4 (2)
Q	0.28 (2)	98 (2)	2.3
R	0.31 (2)	103 (2)	2.7 (2)
S	0.53 (2)	79 (2)	2.2 (2)
Pipe tobacco			
Brand T	2.1 (3)	59 (3)	2.0 (3)
U	2.3 (3)	295 (3)	4.5 (3)
Cigar tobacco			
Brand V	1.08 (3)	139 (3)	5.8 (3)
W	3.0 (3)	54 (2)	1.48 (2)

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[a] The mean deviations from the means computed for replicate analyses of La and As are of the order of ± 10% and for Br of the order of ± 4%.

(ppm) and Sb 0.44-1 ppm, and the other having up to 10 ppm La and 4 ppm Sb. This may indicate different sources for the papers.

A few of the tobaccos were ashed at 900 °C for one hour in a platinum crucible and the ashes were analyzed for several elements. The ashing

Table 3. Determination of chromium, selenium, silver, zirconium, scandium, antimony, zinc, and cobalt in tobacco products by INAA.

Material analyzed	Chromium (ppm)	Selenium (ppm)	Silver (ppm)	Zirconium (ppm)	Scandium (ppm)	Antimony (ppm)	Zinc (ppm)	Cobalt (ppm)
Burley tobacco leaves		2.7 (3)[a]	0.63 (3)		0.64 (3)	10.2 (2)	42 (2)	1.9 (2)
Burley tobacco stalks		45 (2)				0.66 (2)	32 (3)	1.9 (2)
Burley tobacco ashes		34 (2)				47 (3)	61 (3)	1.12 (3)
Cigarette tobacco								
Brand A	1.3 (2)	2.2	0.53 (2)		0.87 (2)	9.3	54	1.01
B	1.4 (2)	4.4	0.046 (2)		0.84 (2)	0.3 (3)	9.8	2.3
C	1.3 (2)	5.8 (2)	2.5 (2)	7.1 (2)	0.59 (2)	14.1 (2)	16 (2)	0.42 (2)
D	1.5 (2)	5.6 (2)	1.26 (2)	11.1 (2)	0.67 (2)	13.7 (2)	17 (2)	0.56 (2)
E	1.2 (2)	3.8	2.2 (2)		0.99 (2)	13.9 (2)		1.19 (2)
F	2.5	2.1	1.62 (2)		1.59 (2)	18.4		1.62 (2)
G	1.3 (2)	1.5 (2)	1.60 (2)	0.12–5.7	0.62 (2)	12.1 (2)	6.3 (2)	0.52 (2)
H	0.81 (2)	ND[b]	2.5 (2)	10.4 (2)	1.20 (2)	23 (2)	ND	0.94 (2)
I	0.24 (2)	1.5	0.64 (2)	16.3 (2)	0.56 (2)	7.4 (2)	25 (2)	0.79 (2)
J	0.36 (2)	ND	0.56 (2)	6.7 (2)	0.53 (2)	25 (2)	25	0.64 (2)
K	1.9 (2)	1.3	1.79 (2)	5.2 (2)	0.71 (2)	15.1 (2)	29 (2)	0.67 (2)
L	0.79 (2)	2.1	1.27 (2)	7.5 (2)	0.57 (2)	14.0 (2)	24	0.75 (2)
M	2.3 (2)	ND	0.35 (2)	10.5 (2)	0.60 (2)	17.4 (2)	46 (2)	0.87 (2)
N	2.5 (2)	ND	3.9 (2)	9.6 (2)	0.78 (2)	38 (2)	29 (2)	0.01 (2)
O	2.5 (2)	1.83	ND		2.5 (2)	20 (2)	42 (2)	0.44 (2)
P	3.4 (2)	1.31 (2)	0.084		1.35 (2)	14.1 (2)	35	0.56 (2)
Q	2.5 (2)	2.9 (2)	1.48		1.25 (2)	11.1 (2)	36 (2)	0.70 (2)
R	1.6 (2)	0.23 (2)	0.10		1.19 (2)	7.8 (2)	4.1	0.53 (2)
S	6.3 (2)	0.14 (2)	0.002		1.86 (2)	7.7 (2)	4.2	0.75 (2)
Pipe tobacco								
Brand T	2.8 (3)	2.5 (3)	0.55		0.22 (3)	8.5 (3)	40 (3)	0.99 (3)
U	2.9 (3)	2.8 (3)	0.93		0.32 (3)	12.5 (3)	11–70	1.66 (3)
Cigar tobacco								
Brand V	6.2 (3)	3.5 (3)	0.07 (2)		0.46 (3)	1.2 (3)	70 (3)	1.65 (3)
W	3.1 (2)	2.6 (2)	0.38 (2)		0.35 (2)	0.52 (2)	38 (2)	1.53 (2)

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[a] Figures in parentheses denote the number of determinations carried out. The mean deviations from the means computed for replicate analyses of Zn, Sc, and Ag are of the order of ± 10%, for Co and Se about ± 15% and, for Sb and Cr of the order of ± 20% and ± 8% respectively.

[b] ND = Not determinable under these irradiation and counting conditions.

Table 4. Determination of trace elements in cigarette paper by INAA.

Material analyzed	Lanthanum (ppm)	Bromine (ppm)	Selenium (ppm)	Scandium (ppm)	Silver (ppm)	Zinc (ppm)	Cobalt (ppm)	Antimony (ppm)	Chromium (ppm)
Cigarette paper									
Brand H	1.85 (2)[a]	17.4 (2)	5.5 (2)	0.32 (2)	1.78 (2)	13.4	0.19 (2)	0.44 (2)	
I	0.36 (2)	13.2 (2)	1.09 (2)	0.32 (2)	0.36 (2)	46 (2)	0.48 (2)	1.54 (2)	
J	0.28 (2)	10.3 (2)	4.6 (2)	0.49 (2)	1.20 (2)	24	0.74 (2)	1.89 (2)	
K	0.27 (2)	6.2 (2)	2.1 (2)	0.29 (2)	0.33 (2)	ND[b]	0.23 (2)	0.73 (2)	
L	0.41 (2)	9.8 (2)	4.0 (2)	0.22 (2)	1.75 (2)	–	0.45 (2)	0.78 (2)	
M	0.44 (2)	4.6 (2)	2.5 (2)	0.56 (2)	1.67	45	0.67 (2)	3.5 (2)	
N	0.45 (2)	6.0 (2)	1.50 (2)	0.075 (2)	0.37 (2)	45	0.47 (2)	0.62 (2)	
O	9.8 (2)	8.4 (2)	1.59 (2)	0.30 (2)	1.56	2.3	1.37 (2)	0.16 (2)	0.90 (2)
P	3.1 (2)	8.3 (2)	1.42 (2)	0.29 (2)	1.45 (2)	ND	1.09 (2)	0.38 (2)	1.82 (2)
Q	3.7 (2)	7.9 (2)	1.91 (2)	0.39 (2)	1.59 (2)	ND	1.34 (2)	0.61 (2)	2.6 (2)
R	4.8 (2)	5.0 (2)	3.5 (2)	0.33 (2)	3.0 (2)	18.6	1.19 (2)	1.35 (2)	1.85 (2)
S	1.88 (2)	14.5 (2)	1.66 (2)	0.37 (2)	1.09 (2)	ND	1.10 (2)	0.85 (2)	2.1 (2)

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[a] Figures in parentheses indicate the number of determinations carried out.

[b] ND = Not determinable under these irradiation and counting conditions.

was carried out only for the tobacco and not for the cigarette paper covering it. It should be noted that this ash will probably differ from normal cigarette ash produced by smoking machines or normal smoking. It would be expected that volatile elements would be depleted in the ashes while the elements forming refractory oxides would be enriched in the ashes. Preliminary data indicate that as expected, most of the Br is lost on ignition. About 75% of the La, 50% of the Se, 90% of the Zn, 96% of the Co and 73% of the Sb is also lost on ignition. The loss of Co in particular is of interest due to the possibility of its loss as $Co(CO)_4$. Many workers have suggested the possibility of this mechanism for volatilization of Ni in tobacco and it well may be true for cobalt. This is interesting in view of the fact that Ni and Co carbonyls are known to induce pulmonary tumors in experimental animals.

This work indicates the feasibility of using nondestructive activation analysis with Ge(Li) detectors in studying concentrations of trace elements in tobacco samples. Studies on the transferrence of these elements into smoke and residual ashes is in progress and when complete should help clarify the picture as to the fraction of toxic and other microelements in tobacco that pass *via* smoke into the lungs.

IV. Acknowledgments

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V. References

[1] Tso, T. C., Botan. Bull. Acad. Sinica **7**, 28 (1966).

SIMULTANEOUS DETERMINATION OF ARSENIC AND COPPER IN WINES AND BIOLOGICAL MATERIALS BY NEUTRON ACTIVATION ANALYSIS

Apostolos P. Grimanis

Chemistry Division
Nuclear Research Center "Democritos"
Athens, Greece

I. Introduction

The importance of copper as an essential trace element in the metabolism of organisms and its role in the flavor of wines [1] together with the widespread use of arsenic as a pesticide in the vineyard with its possible residual toxicity, point to the need for a rapid and accurate method for the simultaneous determination of these two trace elements in wines and biological materials.

Several workers have combined radiochemical separation methods with activation analysis for determining arsenic or copper in biological materials [2-8]. The same elements have been determined in wines only by conventional methods [9-11].

The present paper describes a rapid and simple neutron activation analysis method, based on previously reported work [12-14] for the simultaneous determination of arsenic and copper in wines and biological materials.

II. Experimental

A. Apparatus and Reagents

1. Apparatus

A NaI(Tl) crystal (3 in. × 3 in.) coupled with an Intertechnique 400 channel transistorized pulse-height analyzer model SA-40. A NaI(Tl) well-type scintillation crystal (2 in. × 1.75 in.) connected with a single channel analyzer.

2. Reagents

Analytical reagent grade materials are used:

a. Copper carrier solution: Dissolve copper metal foil in 1% nitric acid to provide a solution containing 10 mg copper per ml.

b. Arsenic carrier solution: Dissolve arsenic pentoxide in 0.05% nitric acid to provide a solution containing 20 mg arsenic per ml.

c. Standard arsenic and copper solution: Prepare a mixed standard solution of arsenic and copper to contain 0.5 mg of arsenic and 1.0 μg of copper per ml by carefully diluting aliquots of the standardized arsenic carrier solution and of the standardized copper carrier solution to the proper volume.

d. Sodium chloride hold-back carrier solution: Prepare an aqueous solution of sodium chloride containing 10 mg sodium per ml.

e. Manganese chloride hold-back carrier solution: Prepare an aqueous solution of manganese chloride containing 10 mg manganese per ml.

f. Rinsing solution: Prepare a mixture of 7.4 M perchloric acid – 1.2 M hydrobromic acid.

B. PROCEDURE

Five ml of each wine were pipetted into polyethylene tubes (15 mm × 58 mm). Aliquots of 5 ml of the mixed standard arsenic and copper solution were also pipetted into identical polyethylene tubes. The tubes were heat sealed and put in the rotating system of the swimming pool type Reactor of Nuclear Research Center "Democritos" and irradiated for 20 hours in a thermal neutron flux of about 1.5×10^{12} $n \cdot cm^{-2} \cdot sec^{-1}$.

Biological materials (150-200 mg) and mixed standard solution (0.5 ml) were placed in smaller polyethylene tubes (10 mm × 30 mm) and irradiated as above. Four ml of the irradiated wine were pipetted into a 150 ml beaker containing 1 ml copper carrier solution, 1 ml arsenic carrier solution and 1 ml of each of the hold-back carrier solutions of manganese and sodium. To the solution 3 ml concentrated nitric acid and 2 ml 70% perchloric acid were added and the beaker was heated until white vapors of perchloric acid were evolved. The resulting solution was made 7 M in perchloric and 1 M in hydrobromic acid and transferred into a separatory funnel containing an equal volume of benzene (10 ml). The arsenic was extracted quantitatively into benzene by shaking for 2 min. The aqueous phase was transferred to a 100 ml beaker for copper separation (see below). The organic phase was washed twice with an equal volume of the rinsing solution and washings were discarded. The arsenic was stripped quantitatively from the benzene into distilled water (10 ml) and the aqueous phase was drawn off into a centrifuge tube containing 1 g sodium hypophosphite, 1 ml sodium hold-back carrier solution and 10 ml concentrated hydrochloric acid solution. The centrifuge tube was placed in boiling water for 1/2 h. After cooling, the mixture was centrifuged, the supernatant liquid discarded and the arsenic precipitate washed with 10 ml of water and centrifuged again. The supernatant liquid was discarded and the metallic arsenic precipitate dissolved into 2 ml of concentrated nitric acid. The solution was transferred to a 5 ml calibrated flask and diluted to volume with distilled water. The arsenic standard was processed in the same manner.

To the beaker containing the copper, 30 ml of water were added and the solution neutralized with ammonia until the characteristic blue copper color appeared. A few drops of 70% perchloric acid were added until the blue color disappeared and then 1.5 ml more. The solution was transferred into a separatory funnel containing 25 ml chloroform and 15 ml 6% aqueous cupferron solution. Copper was extracted into the organic phase by shaking for 2 min. The chloroform layer was transferred to another funnel containing 15 ml of concentrated ammonia and by shaking the funnel, copper was stripped into the ammonia solution.

The solution was drawn off to a centrifuge tube containing 10 ml 3% thioacetamide solution. The mixture was centrifuged, the supernatant liquid discarded and the copper sulfide precipitate washed with 10 ml of distilled water and centrifuged again. The supernatant liquid was discarded and the precipitate dissolved in 2 ml of concentrated nitric acid. The solution was transferred into a 5 ml volumetric flask and diluted to volume with distilled water. The copper standard was processed in an identical manner.

C. ACTIVITY MEASUREMENTS

Take a 3 min count of the volumetric flasks containing the copper and arsenic solutions isolated from the irradiated samples and from the corresponding arsenic and copper standards on the crystal of the scintillation counter. Radiochemical purity was checked in the 400 channel analyzer but contaminants were absent. This was also confirmed by making decay studies and determining the half lives of ^{64}Cu and ^{76}As which corresponded to those reported in the literature.

D. DETERMINATION OF CHEMICAL YIELD

The chemical yield of copper averaged 75%. This determination was made by the reactivation method previously reported [14]. The chemical yield of the isolated arsenic was also determined by reactivation. Aliquots of 1 ml of the arsenic nitrate solution in the volumetric flask were transferred into a 50 ml volumetric flask and diluted to volume with distilled water. Aliquots of 1 ml of this diluted solution were pipetted into polyethylene tubes and 1 ml aliquots of arsenic standard solution (80 μg arsenic/ml) into identical polyethylene tubes. The tubes were heat sealed, wrapped in plastic and irradiated in the pneumatic system for 7 min at a thermal flux of about 2.2×10^{12} $n \cdot cm^{-2} \cdot sec^{-1}$. The irradiated tubes were placed in culture tubes and counted on the crystal of the multichannel analyzer. The relative standard deviation of the reactivation procedure for arsenic is ±3.5%. The chemical yield of arsenic averaged 80%.

III. Results and Discussion

Results of the determination of arsenic and copper in 6 red and 4 white dry wines from different areas of Greece are shown in Tables 1 and 2 respectively. The results given are the mean values of at least triplicate analyses. The reproducibility of the method was checked by analyzing 10 samples of the same wine for arsenic and copper by the proposed method. The overall relative standard deviation was ±5.3% and ±5.7% for copper and arsenic respectively.

Table 1. Simultaneous determination of arsenic and copper in red wines by neutron activation analysis.

Trade name	Origin	Copper μg/ml	Arsenic ng/ml
Candia	Crete	0.11	1.38
Castel Danielis	Patras	0.54	4.55
Chevalier de Rhodes	Rhodes	0.31	4.71
Demesticha	Patras	0.59	7.19
Naoussa Boutari	Naoussa	0.20	3.10
Petit Chateau	Attika	0.17	3.86

Table 2. Simultaneous determination of arsenic and copper in white wines by neutron activation analysis.

Trade name	Origin	Copper μg/ml	Arsenic ng/ml
Caire	Rhodes	0.55	3.07
Kamba	Attika	0.29	4.12
Minos	Crete	0.31	3.93
Santa Elena	Patras	0.18	2.99

A minimum of 0.002 μg of arsenic and 0.005 μg of copper can be determined by this method with a 20 h irradiation.

The method has also been applied for the determination of arsenic and copper in biological materials. Results are listed in Table 3.

Table 3. Simultaneous determination of arsenic and copper in biological materials by neutron activation analysis.[a]

Biological material	Copper $\mu g/g$	Arsenic $\mu g/g$
Animal bone	6.10	2.02
Animal blood	2.38	0.019
Kale	4.64	0.142
Urine[b]	0.30	0.036

[a] Results are means of 4 analyses and referred to dried samples.

[b] Results are given in $\mu g/ml$.

The accuracy of the method was checked by the aid of a biological standard. The amount of arsenic and copper found in the biological standard was 0.14 μg of As and 4.64 μg of Cu per gram of dried matter. These values are in good agreement with the copper and arsenic content found by other laboratories for the same sample [15].

The time required to complete the analysis of both elements is about 1-1/2 h including the reactivation procedure for chemical yield correction and all radioactivity measurements. It has been also found by radiotracer experiments that decontaminations factors greater than 10^6 for zinc, bromine, gold, sodium, antimony and manganese are obtained by the proposed radiochemical separation for arsenic and copper. The only possible interference with the arsenic determination is selenium when present in amounts greater than 10 μg. The selenium content of wines and biological materials is less than this.

The (n,p) and (n,α) reactions produced by fast neutrons were considered for possible interference. Selenium and bromine interfere through the reactions $^{75}Se(n,p)^{76}As$ and $^{79}Br(n,\alpha)^{76}As$. Zinc forms ^{64}Cu according to the reaction $^{64}Zn(n,p)^{64}Cu$. Calculations made by Lukens [16] and Sjostrand [4] show that 1 g of selenium or bromine will form ^{76}As activity equivalent to less than 1 μg of arsenic. Tomura and Higushi [17] found that 1 g of Zn produces ^{64}Cu equivalent to less than 700 μg of Cu. Due to the low concentration of selenium, bromine and zinc in wines and biological materials [18] the possible interference of these elements can be neglected during the determination of arsenic and copper.

The proposed method for the simultaneous determination of arsenic and copper in wines and biological materials is rapid, simple, and accurate.

IV. References

[1] Banick, W. M., and Smith, F., Anal. Chim. Acta. **16,** 464 (1957).

[2] Bowen, H. J. M., and Gibbons, D., Radioactivation Analysis, Clarendon Press, Oxford, 1963.

[3] Lyon, W. S., Guide to Activation Analysis, Appendix A, Van Nostrand, New York, 1964.

[4] Sjostrand, B., Anal. Chem. **36,** 814 (1964).

[5] Heydorn, K., IAEA Symposium on Nuclear Activation Techniques in the Life Sciences, Amsterdam, Netherlands, May 8-12, 1967 Paper No. SM-91/11.

[6] Kaiser, D. G., and Meinke, W. W., Anal. Biochem. **6,** 77 (1963).

[7] Keenan, R. G., Marcus, J. H., and DeVoe, J. R., Proc. 1965 Intern. Conf. Modern Trends in Activation Analysis, p. 243, Texas A&M University, Texas, 1965.

[8] Haven, M. C., Haven, G. T., and Dunn, A. L., Anal. Chem. **18,** 141 (1966).

[9] Levitman, K. Y., Poznyak, S. I., and Vladykina, N. M., Vinodele i Vinogradorstvo S.S.S.R. **17,** No. 5, 9 (1957); C.A., **52,** 2332b (1958).

[10] Malysheva, R. J., Ibid **16,** No. 5, 17 (1956); C.A. **51,** 6940e (1957).

[11] Eschnauer, H., Wein-Wiss., Beih. Fachz. Deut. Weinbau 127 (1957); C.A. **53,** 9565g (1959).

[12] Grimanis, A. P., and Leddicotte, G. W., Trans. Amer. Nucl. Soc. **5,** 195 (1962).

[13] Grimanis, A. P., and Souliotis, A. G., Analyst **92,** 549 (1967).

[14] Grimanis, A. P., Talanta **15,** 279 (1968).

[15] Bowen, H. J. M., Analyst **92,** 124 (1967).

[16] Lukens, M. R., Jr., General Atomic Rept. GA-5075 (1964).

[17] Tomura, K., and Higushi, M., Anal. Chim. Acta **37,** 33 (1967).

[18] Bowen, H. J. M., and Cawse, P. A., AERE-R-4309, Appendix 1, May 1963.

ASPECTS OF LOW TEMPERATURE IRRADIATION IN NEUTRON ACTIVATION ANALYSIS

Dag Brune

AB Atomenergi Studsvik,
Nykoping, Sweden

I. Introduction

Neutron irradiation of the sample while frozen in a cooling device inserted in a reactor channel has been carried out in the analysis of iodine in aqueous samples as well as of mercury in biological tissue and water. The low temperature irradiation technique is in this case adequate for an accurate analysis, inasmuch as iodine is easily evaporated, especially from acid solutions. Iodine is also adsorbed onto plastic containers. Evaporation effects of mercury are strongly pronounced for water solutions and seem to be dependent on the water quality.

Often, in analyses of this kind, a great number of determinations are carried out simultaneously which necessitates the irradiation of a large number of samples in one operation. As regards neutron activation of several aqueous or tissue samples close together, mutual flux perturbation effects may occur giving rise to heterogeneous activation. Such disturbances can, however, be corrected. Similarly a large aqueous or tissue sample gives rise to flux disturbances [1].

Using a special geometrical arrangement during the multiple sample irradiation process as here described the mutual flux perturbation effect can be eliminated.

II. Experimental

A. The Iodine Analysis

Iodine in pharmaceutical plasma solutions (containing 0.9% NaCl) in the concentration range of 50 μg - 50 mg/ml was determined in 0.5 ml samples. A sample arrangement for the simultaneous irradiation of sixty 0.5 ml samples is shown in Figure 1. The holder is made of aluminum. The samples were solidified in a deep freeze refrigerator before being inserted in the cooling device for irradiation. In one series equal amounts of iodine (0.5 mg) were added to sixty 0.5 ml samples in order to investigate the mutual flux perturbation effect. In the irradiation position used the thermal flux gradient was less than 0.5 per cent per cm.

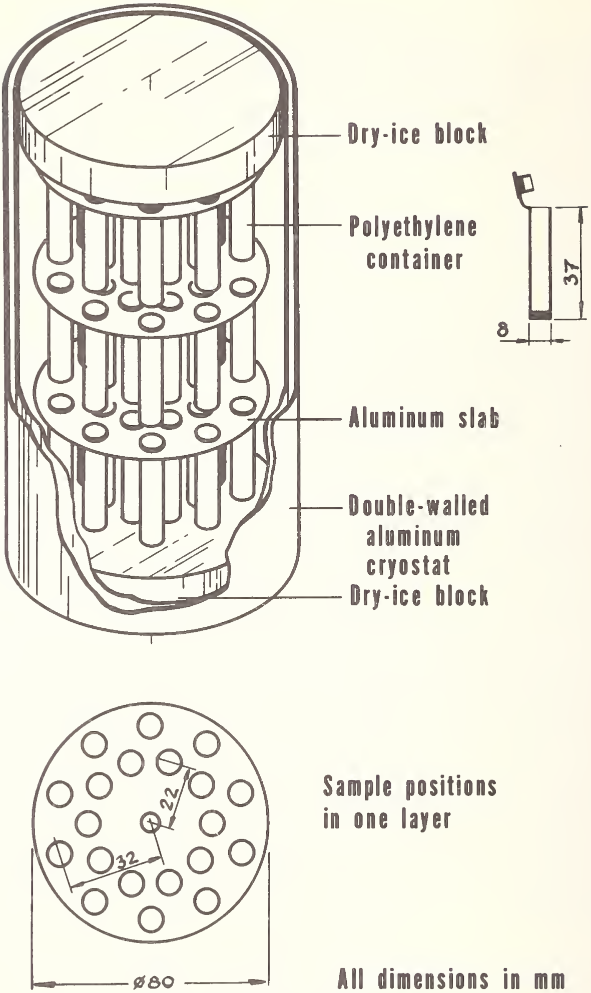

Figure 1. Arrangement for simultaneous irradiation of 60 samples in 3 layers.

The analysis was assayed gamma spectrometrically by means of the nuclide ^{128}I, which was measured directly in the solution without the performance of chemical separations.

B. THE MERCURY ANALYSIS

1-100 ml aqueous samples (rainwater, *etc.*) or fish samples (pike) of 1-10 g contained in polyethylene bottles were solidified like the aqueous iodine samples in a deep freeze refrigerator before being irradiated in the cooling device.

After the activation process the fish tissue was destroyed by immersion in conc. HNO_3 (about 20 ml/10 g fish) and gentle heating for about 20 min in a flask connected to a reflux condenser. About 1 mg $Hg(NO_3)_2$ was added as carrier. The pH of the solution was then adjusted to the region between 1.5 and 2 by neutralization with conc. NaOH. The irradiated aqueous samples were also adjusted to the same pH region by acidification with HNO_3. The mercury activities were then separated from the bulk by means of mercury droplets using an isotopic exchange technique previously described by Kim and Silverman [2]. This technique has recently been modified [3]. The exchange time used depended on the volume of the solution [1]. The analysis was assayed gamma spectrometrically by means of ^{203}Hg.

III. Results and Discussion

A. Cooling Devices

During these experiments dry ice has been used as cooling medium in a double-walled aluminum cryostat inserted in a central channel of a heavy water moderated reactor (Rl). Operation of this device is simple and fairly inexpensive.

The irradiation time available is, however, limited, inasmuch as continuous replenishment of the dry ice material is rather complicated. With the present dry ice cooling arrangement temperatures of about −40 °C were measured in solidified aqueous samples during the irradiation.

B. The Iodine and Mercury Analysis

The geometrical arrangement for low temperature irradiation of sixty 0.5 ml samples simultaneously is shown in Figure 1. With this arrangement no mutual flux perturbation effects were observed. Normalized activities (of ^{128}I) in central and peripheral positions in each of 3 layers are given in Table 1.

Iodine in the concentration range 25 μg - 25 mg in the pharmaceutical solutions was analyzed with standard deviations of the single value less than 5 percent without the performance of chemical separations.

As regards the mercury analysis, low temperature irradiation combined with the fast isotopic exchange technique revealed an overall yield of 98 ± 2 percent (for fish tissue or water).

In a 70 ml rain water sample a mercury content of 0.33 ng/ml was measured. Correction for the flux perturbation effect was carried out by estimation of the flux advantage factor [1].

Dual analysis was made of the mercury content in 3 pike. The result is given in Table 2.

Table 1. Normalized activities (of ^{128}I) in each of the 3 layers.[a]

Layer	Central position	Peripheral position
Upper	0.97 ± 0.05	1.02 ± 0.05
Middle	0.98 ± 0.05	1.00 ± 0.05
Lower	1.00 ± 0.05	0.98 ± 0.05

[a] The values are mean values of 10 samples with standard deviation of the single value. The samples were geometrically arranged according to figure 1.

Table 2. Dual analysis of Hg in 3 pike.

Sample No.	Hg content in μ g/g (wet material)	
1	0.124	0.126
2	0.138	0.139
3	0.141	0.154

IV. References

[1] Brune, D., and Jirlow, K., Radiochim. Acta **8,** 161 (1967).
[2] Kim, C. K., and Silverman, J., Anal. Chem. **37,** 1616 (1965).
[3] Brune, D., Acta Chem. Scand. **20,** 1200 (1966).

DETERMINATION OF THE SPECIFIC ACTIVITY OF COMMERCIAL IODINE-125 PREPARATIONS BY NEUTRON ACTIVATION ANALYSIS

K. Heydorn

Isotope Laboratory
Research Establishment Riso
Roskilde, Denmark

I. Introduction

Proteins such as insulin and serum albumin are often labelled by iodination with iodine-131 or iodine-125 in a carrier-free state. The presence of more than 2-3 atoms per molecule may significantly affect the biological activity of the protein, and most researchers prefer to restrict the iodination to less than one atom per molecule.

The specific activity of the radioactive iodine preparations thus determines the maximum radioactive concentration of the labelled protein. Total iodine in carrier-free ^{131}I was determined by Berson and Yalow [1] by estimating the amounts of singly and multiply iodine labelled molecules from the chloramine-T iodination of insulin, whereas Glover and Shepherd [2] determined the labelling efficiency as a function of added iodine-131 in iodine monochloride iodination.

Helmkamp, Contreras and Bale [3] made direct measurements of total iodine using the iodate-iodide reaction, while Appleby and Spillett [4] used the catalytic effect on the reduction of ceric ions by arsenious acid.

Recently Arino and Kramer [5] determined total iodine in carrier-free ^{131}I by means of an iodide electrode.

Only two single measurements of the specific activity of carrier-free ^{125}I were found in the literature, both reported by radioisotope suppliers [4,5]. To see whether these values were representative of the products supplied to the customers, samples of carrier-free ^{125}I for protein iodination were bought from seven different manufacturers.

A. CHOICE OF METHOD

Iodine-125 for protein iodination is supplied in an aqueous solution containing NaOH or Na_2SO_4 and stated to be in the form of iodide. This may be true for freshly prepared solutions, but in the course of weeks transformation into various iodine-containing compounds of unknown composition gradually takes place [6]. These compounds may be volatile and do not exchange with added iodide even after the addition of Na_2SO_3 or $Na_2S_2O_3$.

The questionable chemical state of the iodine rules out direct application of chemical methods, while extensive chemical treatment to restore a well-defined chemical state, such as digestion and distillation [7], is impracticable for small samples and introduces a blank problem.

It was therefore decided to use instrumental neutron activation analysis for the determination of total iodine, regardless of its chemical state.

II. Experimental

A. Apparatus and Equipment

Danish Reactor DR 2, operating at 5 MW; Multichannel Analyzer, Nuclear Data 160F; Single-channel Analyzer, Nuclear Enterprises 5159; Vibron Electrometer, Electronic Instruments model 33C. All counts were made with a 0.5 mm copper absorber in front of a 3 in. × 3 in. sodium-iodide [NaI(Tl)] scintillation detector, to eliminate contribution from ^{125}I. Calibration was about 6.67 keV/channel, and analyzer dead times near, but not exceeding, 20% were sought.

B. Procedure

Aliquots of 50 or 100 μl are taken from each bottle immediately upon receipt from the supplier and transferred to 1/2 dram polyvials, previously cleaned in HNO_3 and rinsed with deionized water.

The samples are counted for the determination of initial ^{126}I. They are then kept in a freezer at $-20\,°C$ until the $^{125}I : {}^{126}I$ ratio is greater than 10^4.

The samples are now counted for 80 minutes and their total activity measured in a re-entrant ionization chamber connected to a Vibron electrometer. The polyvials are opened, purged with CO_2 for 10 minutes and heat-sealed. The ionization chamber measurement is repeated, and the surface of the polyvials is cleaned with ethanol.

Irradiation for 30 minutes in a thermal neutron flux of 7×10^{12} $n \cdot cm^{-2} \cdot sec^{-1}$ is carried out with the pneumatic tube system of the reactor. An electronic timer starts automatically when the sample leaves the reactor, and initiates the counting at a preselected decay time of 1000 seconds. Counting takes place with a gain of 6.67 keV/channel and a zero shift of 50 channels; a single channel analyzer with the threshold adjusted at 570 keV is connected to the anticoincidence input of the multichannel analyzer and limits the number of channels in the analysis to about 35.

The sample is counted for 2000 seconds clock time and recounted in the subtraction mode one hour later. The resulting difference spectrum is used for the evaluation of the 441 keV photopeak to be compared with a standard of about 500 ng of iodine as HIO_3 irradiated and counted under identical conditions.

The sample is finally counted for 80 minutes 12 days after the end of irradiation. The 386 keV photopeak from ^{126}I is corrected for ^{126}I present before irradiation, the loss of activity by CO_2 purging being taken into account; the resulting photopeak area is compared with a standard of 229 μCi ^{125}I irradiated and counted under identical conditions.

III. Results and Discussion

A. RESULTS

Results of the determination of ^{125}I are presented in Table 1 along with the standard deviations based on counting statistics. Photopeak areas from 386 keV gamma rays from ^{126}I determined before and after irradiation are converted to gamma quanta per second by means of an absolutely standardized ^{113}Sn solution emitting 393 keV gamma rays. All disintegration rates are corrected to the end of irradiation assuming an ^{126}I half life of 12.8 days.

The loss of activity by purging with CO_2 is limited to a few percent with the exception of sample G, which lost almost 20%. This particular sample was supplied in 0.02 *M* Na_2SO_4, while all the others were in NaOH solution.

Results of determinations of ^{126}I concentrations in the samples immediately after receipt are presented in Table 2 along with sample

Table 1. Determinations of iodine–125 by neutron activation analysis.

Supplier code	Days after receipt	386 keV γ/sec before irradiation	Activity loss by CO_2 purging (%)	386 keV γ/sec after irradiation	386 keV γ/sec[a,b] from ^{125}I	Iodine–125 (ng)
A	101	305	1.5	1913	1617	80.9 ± 1.2
B	100	63	0.7	326	263	13.2 ± 0.2
C	92	36	6.0	484	453	22.6 ± 0.5
D	114	1544	1.1	3044	1494	74.7 ± 1.2
E	113	1359	4.7	2408	1102	55.1 ± 0.9
F	99	7	6.2	122	114	5.7 ± 0.2
G	98	734	18.7	1633	1087	54.4 ± 0.9

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[a] Corrected for minor differences in irradiation conditions.

[b] All activities refer to the end of irradiation.

Table 2. Determination of total iodine and specific activity of iodine–125 solutions.

Supplier code	Iodine–126 concentration μCi/ml	Sample volume μl	Iodine–125		Iodine–127 μg	Total iodine μg	Specific activity mCi μg
			mCi	μg			
A	133	50	4.51	0.259	0.139 ± 0.033	0.398	11.3 ± 0.9
B	28.7	50	0.73	0.042	0.017 ± 0.012	0.058	12.5 ± 2.6
C	5.18	50	1.14	0.066	0.101 ± 0.017	0.166	6.9 ± 0.7
D	1215	50	4.85	0.279	0.031 ± 0.037	0.310	15.7 ± 2.0
E	1145	50	3.54	0.203	0.047 ± 0.019	0.250	14.2 ± 1.1
F	0.74	100	0.31	0.018	0.023 ± 0.004	0.041	7.7 ± 0.7
G	227	50	2.94	0.169	0.282 ± 0.010	0.450	6.5 ± 0.2

Note: All activities refer to the time of receipt of samples.

volumes. In the conversion from 386 keV gamma quanta per second to μCi of ^{126}I an abundance of 34% was assumed.

Determination of ^{127}I by means of a peak location program described by Yule [8] gave positive identification in three cases. Careful study of the spectra resulted in the remaining figures for ^{127}I given in Table 2 along with their standard deviations based on counting statistics.

The ^{125}I determinations from Table 1 are corrected back to the time of receipt assuming a half life of 60 days. The figures are given in Table 2 in μg as well as in mCi with a conversion factor of 17.4 mCi/μg.

Total iodine is now the sum of the masses of ^{125}I and ^{127}I : ^{126}I has a mass of only 12.3 ng/mCi and can be completely ignored. Finally the specific activity of the product is presented in the last column in Table 2 as the ratio between the ^{125}I activity and total iodine.

B. DISCUSSION

The specific activities of the seven different commercial iodine-125 preparations were found to range from 6.5 to 15.7 mCi/μg, corresponding to 37.5 – 90% of that of the truly carrier-free product. With the exception of sample G, high ^{126}I : ^{125}I ratios, indicating freshly made ^{125}I, gave high specific activities.

Appleby and Spillett [4] found a specific activity of ^{125}I from the Radiochemical Centre of 11.0-11.4 mCi/μg which is in excellent agreement with the corresponding value of sample A.

Arino and Kramer [5] found 16.6 mCi/μg, which is in very satisfactory agreement with the corresponding value of sample D of this investigation.

The present method is not subject to errors from the unknown chemical state of iodine-125 in carrier-free solution, and so provides an important check on the accuracy of other methods. Only small samples are needed, but the time required for decay of ^{126}I makes the method unsuitable for regular production control.

III. Acknowledgments

The author is grateful to I. Funck-Hansen for his excellent work in the counting of these special samples, and to Ulf Jacobsen for supplying a calibrated ^{125}I sample.

Thanks are also due to the Northern European University Computing Centre at Lundtofte for making the IBM 7094 available for the computations.

IV. References

[1] Berson, S. A., and Yalow, R. S., Science **152,** 205 (1966).
[2] Glover, J. S., and Shepherd, B. P., Nature **212,** 285 (1966).
[3] Helmkamp, R. W., Contreras, Ma. de los Angeles, and Bale, W. F., J. Nucl. Med. **7,** 491 (1966).
[4] Appleby, A., and Spillett, R. E., U.K.A.E.A. Memorandum RCC-M 210 (1967).
[5] Arino, H., and Kramer, H. H., Nucl. Applic. **4,** 356 (1968).
[6] Jacobsen, U., private communication.
[7] Bale, W. F., Helmkamp, R. W., et al, U.S.A.E.C. R & D Rept. UR-604 (1962).
[8] Yule, H. P., Anal. Chem. **38,** 103 (1966).

CHAPTER 3

FORENSIC AND ARCHAEOLOGICAL APPLICATIONS

Synopsis of Discussions

ROBERT E. JERVIS, *Chairman*

University of Toronto
Toronto, Canada

Session 4 consisted of the very interesting presentation and discussion of (1) four papers dealing with the analyses of oil paintings, ancient coins and pottery of archaeological interest, and (2) a group of five papers reporting activation techniques for examination of forensic samples: hair and other tissues, ballistic materials and soils, and actual applications to crime investigations and poisonings. While the scope of these papers extended from the time of historical antiquity up until very recent new applications in crime detection, they had in common the approach of attempting to reveal the origin or movement of materials through characteristic trace element content or detection of adulteration.

Most of the authors reported the use of nondestructive instrumental activation analysis [both NaI and Ge(Li)] partly because it had been necessary to preserve the specimens in a relatively intact although slightly activated condition or to handle a large number of similar samples on a semi-routine basis. For example, both Dr. Meyers from the Institute of Applied Nuclear Research, Amsterdam, and Dr. Gibbons from Wantage Laboratory of the United Kingdom carried out analyses on coins which had to be returned to museum collections. It is noteworthy that most of these papers dealt with actual practical applications of the techniques rather than the reporting (as in the past) of academic efforts to show that activation analysis could have a great potential to revolutionize these fields of popular interest. This further stage in the maturity of the technique received comment in the discussion period.

There were several topics of unusual interest arising from these papers; both Gibbons and Meyers reported on trace elements for the dating and the characterization of old coins. In the former study more than 700 coins were analyzed for silver content in groups of 25 by means of thermal neutron activation and sodium iodide spectrometry. Coins and interleaving silver foil monitors were corrected for self-shielding and flux gradient, and the silver content calculated by a computer. The silver content of the coins varied in a consistent manner during the seven centuries of their production. The latter study involved charged particle activation analysis of Zn, Cu, Ag and Pb impurities in gold and silver coins, and the effective beam intensity during activation was monitored by means of thin foils placed in front of the coin.

The trace element content, particularly of manganese, silver, and antimony in white pigment from old oil paintings was examined an activation method involving specific radiochemical separation techniques according to a report by Lux. In earlier work the content of Zn and Cr in white pigment was shown to be variable according to the date of the original painting but this paper provided a more detailed study of trace elements in old pigments. In this way the approximate date of a painting and the probable geographical location of the painter could be deduced by comparison with paintings of known origin, and in addition, a recent forgery bearing many resemblances to old paintings could be detected since the white pigment on the paintings was relatively pure with respect to these pigment impurities which occurred at higher concentration several centuries ago.

Sayre reported on a trace element comparison of two potteries of similar appearance found both in England and in the eastern coast of North America. An instrumental activation determination of several trace element ratios was made which showed strong similarities between some samples from the two sources, suggesting that the English pottery many have been brought early to America.

The latter group of papers in this session dealt with activation applications in forensic science and there was considerable interest in, and discussion of these papers.

A paper from the Internal Revenue Service, Washington, contained data on a trace element survey of soils sampled over specified grid patterns in several remote sites and a statistical interpretation of the results led the authors to conclude that an analysis for 10 to 12 trace elements in two soil samples should permit decision as to common source of the two soils with a probability of approximately 2 in 10^6 that a similar trace element composition should occur accidentally in two unrelated soil samples. There were some questions raised as to the certainty of this conclusion and particularly to inquire into the extent of the variation within the same immediate area from which replicate soil samples are obtained. A similar discussion arose concerning the certainty of comparing hair specimens through instrumental activation analysis. In his paper, Perkons of the Ontario Centre of Forensic Sciences outlined activation applications to several types of evidence material from suspected crimes. Based on comparisons of gamma detectors he reported that more than twice as many nuclides (*i.e.* up to 23) could be determined in small hair specimens using a Ge(Li) detector compared to those detected by NaI spectrometry. He also reported on the detection of minute residues in skin resulting from electrocution and contact with an electrical conductor. Further data indicating the detection of bullet material transferred to bone and suggesting instrumental means of characterizing narcotic materials were also presented. Lukens of Gulf General Atomic presented results of the activation analysis of evidence materials from several actual criminal cases which had been undertaken for presentation in the court. These cases involved hair, gun shot residues, bullet fragments and paint pigments. The scope of this paper was restricted to an outline of the details of actual criminal case investigation and did not attempt to summarize the background research on many samples of these same materials which had served as a basis for these applications. A number of questions concerning the validity with which it could be established that a person had recently fired a gun arrived at by measuring microgram deposits of antimony and barium on a suspect's hands would probably not have arisen had this information been available.

Two final papers on this session dealt with the forensic use of hair analysis. A study of arsenic content in hair from persons exposed occupationally to arsenical dust was reported by Houtmann of Delft, and results indicated that hair must be taken through a precleaning operation since elements such as arsenic judged to be contained within hair may in fact, only be attached to the surface and may be removed by certain washing or leaching operations. A study reported by Williamson of the University of Virginia concerned comparison of the sensitivity of spark source mass spectrometry and instrumental neutron activation analysis with a Ge(Li) detector. It is reported that while approximately 20 nuclides can be measured with some precision by activation analysis, about 29 elements were detected by the mass spectrometry technique, and that while the studies had required rather large quantities of hair, it was anticipated that future methods could extend to smaller quantities and hence of some practical value in actual crime detection.

A general discussion followed about the degree of certainty with which one could state in a court of law on the basis of trace element analysis that the samples being compared came from the same source or did serve to connect the criminal with the crime. Statistical information on the similarity between samples from the same source and the extent of the differences among samples from different sources are required to justify such interpretation and it was felt that at present, such information was available for only a few materials.

An opinion was expressed that considerable series of analyses should be carried out with a statistically-significant population of samples representing a wide variety of sources so that physical analysis could be made of the extent of variation among samples of the same source by comparison of the variations characteristic of distinct different sources.

However, it would seem that, at the present time, activation analysis is being required to provide more positive answers for the courts than is provided by other methods in common use by forensic scientists or is available from the testimony of eye witnesses to a crime. Certainly the answers provided through activation analysis should be definitive but it would seem unreasonable at this point to require possible source and/or identity of case samples in terms of probability of their batching which is out of all proportion to the other techniques presented in court.

INVESTIGATIONS ON THE AGE AND PLACE OF ORIGIN OF PAINTINGS BY NEUTRON ACTIVATION ANALYSIS[1]

F. Lux, L. Braunstein and R. Strauss

Institut fur Radiochemie
der Technischen Hochschule Munchen
8046 Garching bei Munchen, Germany

I. Introduction

For the scientific investigation of paintings only very small samples can be taken. Therefore micro analytical methods must be applied even for the determination of the main constituents [1]. In spite of the small samples available, the high sensitivity of activation analysis makes possible a treatment of a problem which exceeds the usual analysis of pigments: to determine *trace elements* in white lead (2 $PbCO_3 \cdot Pb(OH)_2$, principal component of all the pigments) expecting that from different distribution patterns some conclusions relating to the history of art could be drawn.

Emission spectrographic work done by H. Kuhn, Doerner- Institut in Munich, gave some indications for the existence of such correlations [2]. Small amounts of copper and silver which can easily be detected by emission spectrography were found in white lead from old paintings but not in white lead from newer ones. Furthermore it was recognized that copper was detectable in white lead from paintings of Old German Masters (Altdorfer, Durer) but not silver. Emission spectrography is not sensitive enough to give more than this kind of qualitative information. By using activation analysis quantitative determinations of copper, silver, and other trace elements, too, should be possible.

Houtman and Turkstra [3] have determined trace elements in white lead from Flemish and Dutch paintings. Their principal observations were: a noticeable decrease of chromium in the middle of the 17th century and a noticeable decrease of the other trace elements in the middle of the 19th century; white lead of the last decades often contains rather high amounts of zinc. So they obtained a time scale in a similar way as De Wild [1] and Laurie [4] did earlier considering the occurrence of the different pigments.

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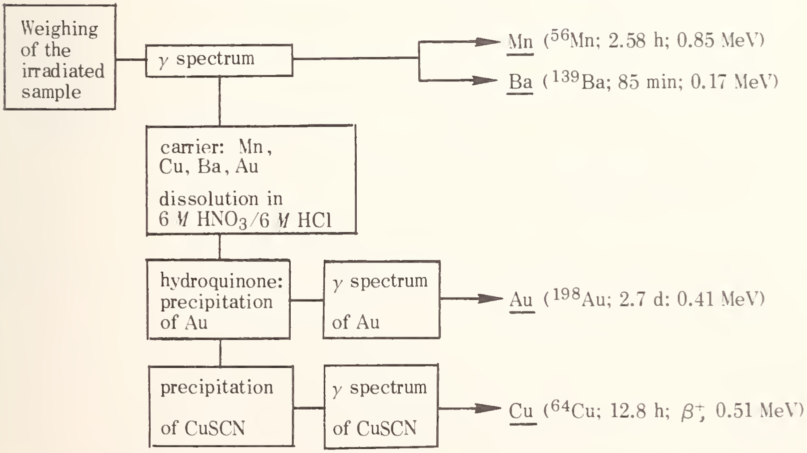
[1] This work was supported by the Deutsche Forschungsgemeinschaft.

II. Experimental

In order to avoid contamination from other pigments the samples of white lead were taken from distinctive white spots of the paintings, *e.g.* spots where light is indicated in the painting. Sample weight usually was less than 1 mg; in some cases only 10 to 20 μg were available. Each sample is divided into two parts: one for short time irradiation, one for long time irradiation. The samples must be present in the form of small grains, otherwise these small amounts cannot be handled. After irradiation the samples have to be removed mechanically from the containers in order to avoid erroneous results caused by dissolving of activated metal traces from the container surface.

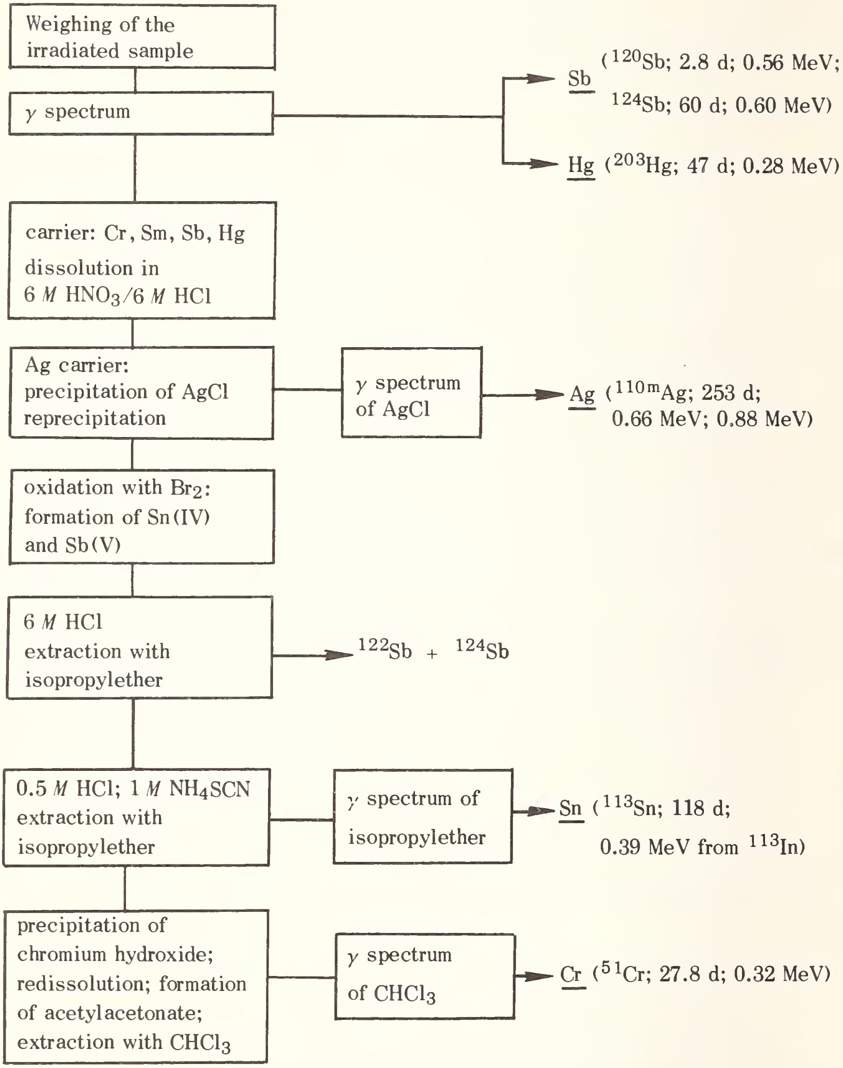
The determined trace elements were: Cr, Mn, Cu, Ag, Sn, Sb, Ba, Au, Hg. Samples were irradiated at Forschungsreaktor Munchen (FRM). The formed radionuclides were determined by combination of radiochemical separation and gamma spectrometry according to the schemes presented in Table 1 and Table 2. The method does not include determination of chemical yield. The reproducibility of the separation is shown by Table 3. Since one cannot expect a constant percentage of the binder, the lead percentage of the samples is determined by anodic stripping polarography. To the amount of lead determined in this way the percentage of trace elements is referred. The aliquot taken for the determination of lead can be one tenth of the sample only since the amounts of trace elements present sometimes are near the detection limit.

Table 1. Separation scheme for short time irradiated samples, determination of manganese, copper, barium, gold.


Weighing of the irradiated sample
γ spectrum
Mn (^{56}Mn; 2.58 h; 0.85 MeV)
Ba (^{139}Ba; 85 min; 0.17 MeV)
carrier: Mn, Cu, Ba, Au
dissolution in 6 M HNO_3/6 M HCl
hydroquinone: precipitation of Au
γ spectrum of Au
Au (^{198}Au; 2.7 d: 0.41 MeV)
precipitation of CuSCN
γ spectrum of CuSCN
Cu (^{64}Cu; 12.8 h; β^+, 0.51 MeV)

Note: Sample is sealed in polyethylene and irradiated 4 hours at 5×10^{12} [n · cm^{-2} · sec^{-1}].

Table 2. Separation scheme for long time irradiated samples; determination of chromium, silver, tin, antimony, mercury.



Note: Sample is sealed in silica and irradiated 500 hours at 2×10^{13} [$n \cdot cm^{-2} \cdot sec^{-1}$]

Table 3. Radiochemical separation; reproducibility in test analyses.

No.	Percent yield Chromium	Copper	Silver	Tin	Gold
1	81.4	93.6	89.1	83.2	97.1
2	85.3	93.4	93.2	98.2	98.3
3	83.2	93.5	92.5	81.3	92.8
4	79.8	99.8	91.9	81.9	97.3
5	82.5	99.1	95.3	82.0	96.4
mean value	82.4	95.9	92.4	83.3	96.4
std. dev. s	±2.1 %	±3.4 %	±2.3 %	±2.9 %	±2.1 %

Note: Mn, Sb, Ba, Hg; direct measurement without chemical separation.

The standard deviations of these lead determinations were ± 3.4% for 5×10^{-7} g and ± 2.4% for 3×10^{-6} g lead. Table 4 shows the detection limits found under given conditions for the different trace elements. Results obtained for samples taken from different parts of the same painting are listed in Table 5.

In the case of long-time irradiated samples the possibility of instrumental analysis was tested using a Ge(Li) detector (8 cm³). The

Table 4. Detection limits for procedure including chemical separations, 800 minutes counting period.

Element	Detection limits (g)	Detection limits (ppm) sample, 10 μg	sample, 100 μg
Chromium	2×10^{-10}	20	2
Manganese	1×10^{-11}	1	0.1
Copper	1×10^{-10}	10	1
Silver	1×10^{-10}	10	1
Tin	3×10^{-10}	30	3
Antimony	1×10^{-11}	1	0.1
Barium	1×10^{-9}	100	10
Gold	1×10^{-11}	1	0.1
Mercury	5×10^{-11}	5	0.5

Table 5. Silver and antimony contents in white lead samples from different parts of the same painting.

JOACHIM VON SANDRART:	Weight	ppm	
"Fischzug Petri"	(μg)	Silver	Antimony
from the middle of the painting	57.5	72	146
from the fish, middle of the painting	386.7	69	114
from the right fish on the basket, right side of the painting	52.3	67	137

obtained detection limits are shown by Table 6. It is evident that chromium and tin cannot be determined in this way. A determination of silver by instrumental analysis might be possible, but only if percentage of silver as well as weight of sample are comparatively high. (If a NaI(Tl) detector is used the 0.56 MeV and 0.60 MeV peaks of ^{122}Sb and ^{124}Sb—always being very high in the case of white lead—strongly interferes with the 0.66 MeV peak of ^{110m}Ag which then cannot be measured at all. As shown in section III the silver content is important for conclusions relating to the history of art). The problem will be investigated once more using a larger Ge(Li) detector.

Table 6. Detection limits for instrumental analysis with Ge(Li) detector (8 cm^3), 800 minutes counting period.

Element	Detection limits (g)	Detection limits (ppm)
		sample 100 μg
Chromium	1×10^{-8}	100
Silver	3×10^{-9}	30
Tin	1×10^{-8}	100
Antimony	2×10^{-10}	2
Mercury	6×10^{-10}	6

III. Examination of Paintings

A. DISTRIBUTION PATTERN OF TRACE ELEMENTS IN WHITE LEAD AS A MARK OF REGIONAL AND INDIVIDUAL ORIGIN

The first series of analyses involved paintings of (1) Flemish and Dutch Masters from the 16th and 17th century, viz Rubens, Vermeer, Hemessen, Janssens, Roymerswaele, and (2) Venetians from the 16th century, *viz* Tizian, Tintoretto. The results are presented in Figure 1. In the case of manganese, silver and antimony the trace content is clearly dependent upon the region where the picture was painted [2]. These differences in trace contents of white lead from regions in the South of the Alps and from regions in the North of the Alps was also found within paintings of one artist, *viz* two paintings of Tiepolo (Fig. 2). So, in principle activation analysis can help in finding an answer to the question of whether a certain painting of an artist originated in Italy or in the North of the Alps. This question often arose in the European history of art.

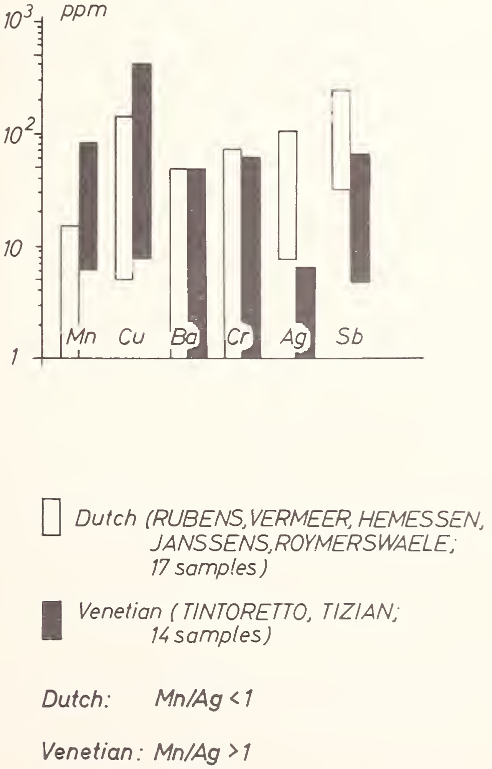


Figure 1. Traces in white lead of Flemish – Dutch and Venetian paintings.

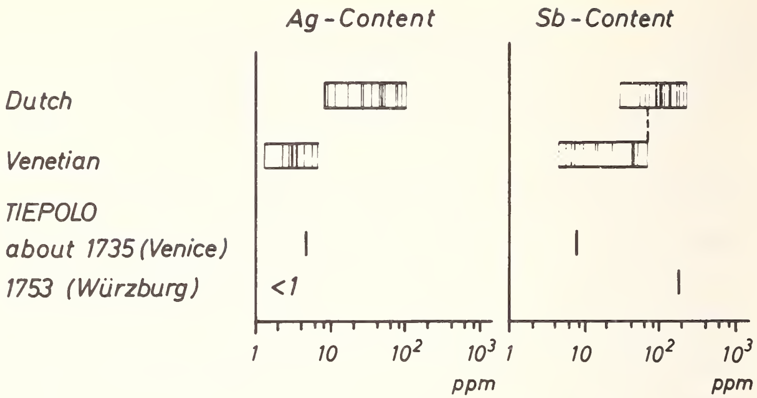


Figure 2. Silver and antimony contents in white lead of Tiepolo paintings, "The Adoration of the Holy Trinity by Pope Clemen" (painted in Venice) and "The Worshipping Kings" (painted in Wurzburg).

In a second series of analyses a selection of paintings was investigated which were created by artists mostly working at the Munchner Hof or elsewhere in Southern Germany. Again, significant differences in the silver and antimony percentages were obtained which could be taken for classification of white lead (Fig. 3, Table 7). Comparison with the above mentioned investigations [2] shows that type 2a is identical with Venetian white lead. This is not surprising since we know from old documents [5] that in those days the Munchner Hof really obtained white lead from Italy. In the paintings from Southern Germany "Flemish–Dutch white lead" (2c, 3b, 3c) and the white lead used by Tiepolo in Wurzburg (3a, also compare Fig. 2) were also found.

An additional result of the second series of analyses is that for the first time the distribution patterns of trace elements in white lead could be taken as marks of individual origin for pictures which were painted by artists who worked in the same place at the same time. The examined pictures painted by Candid contained only white lead of type 2a which was not found in any one of the examined Fischer paintings (Fig. 4). The noteworthy point is that Fischer's paintings formerly were affiliated to Candid. In the meantime the error has been known by historians of art [6], and it is a very interesting fact that activation analysis confirmed their revised opinion.

B. TRACE CONTENTS IN WHITE LEAD AND DATING

From the results of our analytical investigations of old paintings no clear conception for dating could be deduced. A tentative correlation

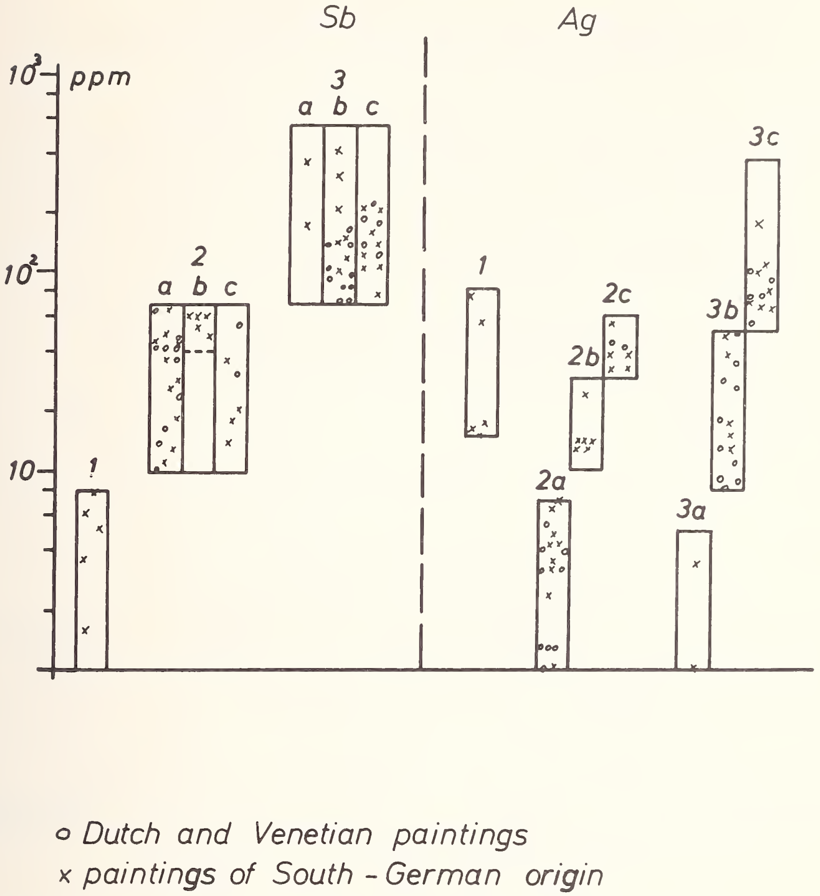


Figure 3. Different types of white lead defined by the antimony and silver contents; o=Flemish—Dutch and Venetian paintings; x=paintings of South—German origin.

between different types of white lead and period of origin is presented in Table 8.

C. Detection of Forgeries

By means of distribution patterns of trace amounts, white lead produced nowadays can be distinguished from white lead used by old masters [2,3]. As mentioned above Houtman and Turkstra [3] found rather high amounts of zinc in white lead from the 20th century. The silver and antimony contents in white lead produced in our days are very

Table 7. Different types of white lead defined by the antimony and silver content.

Type of white lead	Antimony (ppm)	Silver (ppm)
1	< 8	15 – 75
2 a (Venetian)	10 – 70	< 7
2 b	10 – 70	10 – 30
2 c (2 of RUBENS paintings)	10 – 70	>30
3 a (TIEPOLO Würzburg)	>70	< 5
3 b (Dutch)	>70	8 – 50
3 c (Dutch)	>70	>50

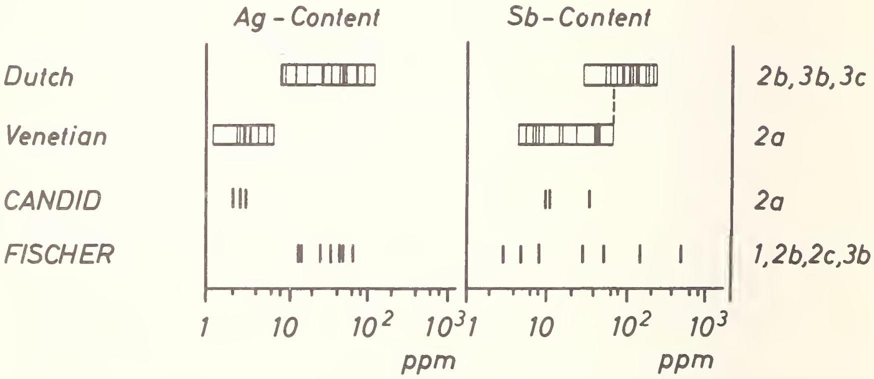


Figure 4. Silver and antimony contents in white lead of pictures painted by P. Candid and J. G. Fischer.

low if compared with those in white lead from old Flemish–Dutch paintings, but it is to be mentioned that old Venetian white lead also contains small amounts of these trace elements only (Fig. 1). In the samples of new white lead which we analyzed, the copper content was very low (<1 ppm) while more than 5 ppm were found in all samples taken from old paintings. These possibilities for discriminating new white lead from an old one can help to uncover forgeries. As an illustrative example a picture is taken which was painted in Old Flemish–Dutch manner by a well known forger of the 20th century (see Table 9).

Table 8. Tentative correlation between different types of white lead and period of origin.

1, 2 c:	until 1640
2 a:	from 1615
3 c:	from 1640
2 b:	from 1670
3 b:	entire period[a]

[a] Chromium content in 3 b, > 10 ppm before 1625, not detectable (< 1 ppm) later on.

Table 9. Silver and antimony content in a forgery of the 20th century.

"Christ and Magdalen"

painted in the Old Dutch manner

	ppm	
	Silver	Antimony
Dutch 16th and 17th century	8 – 103	50 – 230
Forgery 20th century	<7	<1.3

IV. References

[1] Wild, A. M. de, The Scientific Examination of Pictures, London, 1929.

[2] Lux, F., and Braunstein, L., Z. Analyt. Chem. **221,** 235 (1966).

[3] Houtman, J. P. W., and Turkstra, J., Radiochemical Methods of Analysis, Vol. I, I.A.E.A., Vienna, 1965, p. 85.

[4] Laurie, A. P., Analyst **55,** 162 (1930).

[5] Staatsarchiv fur Oberbayern, HR II, Fasc. 279, Nr. 4 Munchen, 1586.

[6] Knuttel, B., Zur Geschichte der Munchner Residenz I, Munchner Jahrbuch der bildenden Kunst 1967, Prestel, Munchen, 1968.

AN INVESTIGATION OF THE SILVER CONTENT OF ROMAN COINAGE BY NEUTRON ACTIVATION ANALYSIS

D. Gibbons and D. Lawson

Wantage Research Laboratory (AERE)
Wantage, Berkshire, England

I. Introduction

A selection of silver coins, minted during the period 27 BC (Augustus) to 275 AD (Aurelian), have been examined in order to determine their silver content. A large number of coins have been analyzed to give representative results for the short reigns of various Emperors and for periods of economic difficulty usually brought about by war. Since the Roman currency was notionally based on pure silver, representative silver analyses enable the debasement of the coinage to be followed and the course of inflation to be assessed [1].

Neutron activation analysis was chosen as the analytical method largely on the basis of ready application as a nondestructive method which can be used to study a large number of samples and which, in comparison with x-ray fluorescence and spectrographic methods, will give a bulk silver content free from errors due to surface leaching or enrichment [2], and will especially show up those coins which were silver plated [3]. Although activation analysis has already been used for the measurement of silver and other elements in ancient coins [3,5], it was rejected by Carter [2] as being too expensive. The technique has therefore been studied with a view to reducing costs as much as possible, and the effects of various sources of error have been examined.

II. Experimental

A. Irradiation

Activation analysis is more than adequately sensitive for the measurements because the silver contents lie in the range 3-70%. Even so, because of the high induced activity expected from copper, it was decided to measure the silver *via* long-lived silver-110m after allowing short-lived activities to decay. At these silver concentrations however, an irradiation of about 10 sec was all that was required at a neutron flux of $10^{12} n \cdot cm^{-2} \cdot sec^{-1}$ so that the build-up of long-lived matrix activity was minimized. This was important in regard to the subsequent storage of the radioactive coins.

This short irradiation time resulted in low irradiation costs, but it was decided to reduce these costs even further by fully utilizing the available irradiation container volume. It was possible to irradiate about 25 coins simultaneously, but this naturally enhanced the flux depression within the coins [4]. However, the coins were irradiated with interleaved thin silver foil standards, separated with paper spacers to prevent transfer of silver from the foils to the coins, and the silver contents were calculated by comparing the coin activities with the mean of the activities of the foils on either side. This effectively compensated for self-shielding errors by subjecting the standards to the same flux perturbations as the samples and also compensated for flux variations, due to external effects along the length of the irradiation container. This was shown to give results which were independent of the position of an individual coin, provided that a dummy 'coin' was placed at each end of the coin-foil stack to reduce end effects.

B. Counting

A preliminary examination of typical coins was made using a Ge(Li) semiconductor gamma-ray spectrometer to check for the presence of other long-lived activities such as antimony-122 and antimony-124 which could interfere in the measurement of the 0.66 MeV silver gamma ray, and manganese-54 (produced from iron) which could interfere in the measurement of the 0.89 MeV silver gamma ray. The presence of antimony and iron in some ancient coins has been reported [3,4].

Manganese-54 was not detected in any of the coins examined, but in some cases the presence of antimony was confirmed. Although this activity did not constitute as interference in Ge(Li) measurements, the counting time using this detector was prohibitive since the volume of the detector then available was only 5 cm^3, and all subsequent routine measurements were made with a conventional NaI(Tl) gamma-ray spectrometer. When results at both 0.66 and 0.89 MeV were in agreement within counting statistics, the silver content was expressed as the mean of the two results; if the results were not in agreement, only that for 0.89 MeV was used, and in some cases a detailed investigation of the spectrum was made with the Ge(Li) spectrometer.

Possible errors during counting due to differential gamma-ray self-absorption between coins and foils and to geometric effects due to a foil being effectively closer to the detector because of its smaller thickness, were assessed experimentally and shown to be in the order of 1.5% at 0.66 MeV and 1% at 0.89 MeV. Corrections for these effects were therefore made on this basis.

C. Data Treatment

Because of the large number of coins involved, it was decided to use computer treatment of the gamma-ray spectrometer data, but full least squares fitting was ruled out because of the need to know details of all components of the spectra. An alternative procedure available in the program GASP [6] then in use enabled individual peak areas to be evaluated by fitting a combination of a Gaussian distribution and a linear distribution to the data. This was satisfactory at 0.66 MeV, but was impractical at 0.89 MeV because this peak is in fact a triplet and the statistical error associated with the total area from three separate fits was unacceptable. It was established that the method of Covell [7] could be applied to the overall 0.89 MeV peak when using the NaI(Tl) detector and it had already been demonstrated that, provided peak drift was reduced to less than 5% of the full width of the peak at half maximum height, the reproducibility of relative activity measurements on nonenergetic peaks was superior to the Gaussian fitting method [8].

A computer program was written which (a) checked the validity of the punched paper tape data, (b) located the position of the silver peaks to within 0.1 channels, (c) adjusted the data to center the peaks exactly on previously defined reference channels, (this adjustment was made on a linear basis, even though the original shift was probably due to gain changes, since the shift never amounted to more than 2 or 3 channels), (d) calculated a fixed fraction of the peak area by the method of Covell [7], (e) calculated the silver content using the mean of the fractional areas for the foils on each side of a coin, (If a coin spectrum included invalid data in the region of the peaks, the spectrum was rejected. If a standard was similarly rejected or was accidentally omitted, then the standards on either side of the two coins were used.) and (f) tabulated all the results. The average total computing time per coin was about 5 seconds.

III. Results

As a check on the overall accuracy, a series of silver sixpences dated 1872-3 from the reign of Queen Victoria, and dated 1921-5 from the reign of King George V were analyzed using the same procedure as for the Roman coins. The sixpences, which were in near mint condition, were assumed to contain the published assay silver concentrations of 92.5% and 50.0% respectively. The mean concentrations by activation analysis and the associated standard errors (95% confidence level) were (92.2±1.8)% and (50.6±0.4)% respectively. The standard deviations of individual measurements (95% confidence level) were ± 5.0 and ± 2.4 respectively (*i.e. ca.* 5% of content).

In all, some 700 coins were analyzed by the activation method. The silver contents varied from 3 - 70%, and some typical results are shown plotted against probable date of minting in Figure 1.

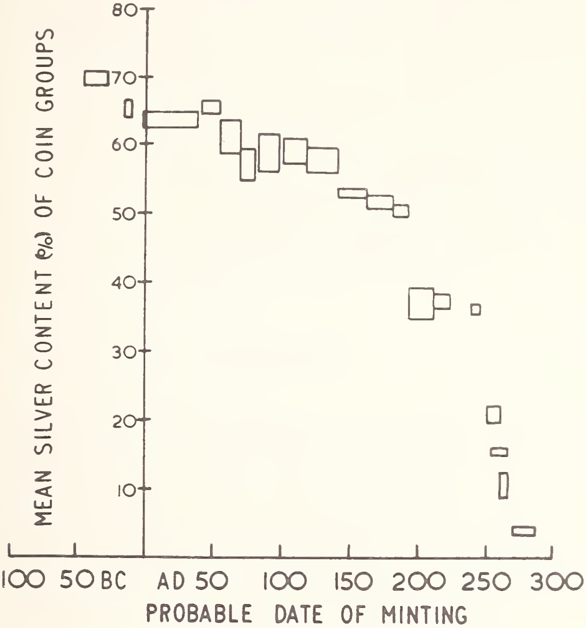


Figure 1. Average silver content of Roman coins as a function of probable date of minting.

IV. Conclusions

Neutron activation analysis has been shown to be an economical and reliable method for the nondestructive measurement of the silver content of valuable coins. Because of the ability of this method to provide the average silver content through the depth of a coin, it can provide more meaningful results than other instrumental techniques.

V. References

[1] Tyler, P., Personal communication.
[2] Carter, G. F., Anal. Chem. **36,** 1264 (1964).
[3] Aitken, M. J., Emeleus, V. M., Hall, E. T., and Kraay, C. M., Proc. Conf. "Radioisotopes in the Physical Sciences and Industry", (Copenhagen 1960), I.A.E.A. Vienna, 1962, Vol. II, p. 261.
[4] Das, H. A., and Zonderhuis, J., Rec. Trav. Chim. **85,** 837 (1966).
[5] Zuber, K., C.N.A.E.M., 21, (1965).
[6] Salmon, L., Proc. Conf. "Radiochemical Methods of Analysis" (Salzburg (1964), I.A.E.A. Vienna, 1965, Vol. II, p. 125.
[7] Covell, D. F., Anal. Chem. **31,** 1785 (1959).
[8] Gibbons, D., and Olive, G., Unpublished.

NONDESTRUCTIVE ACTIVATION ANALYSIS OF ANCIENT COINS USING CHARGED PARTICLES AND FAST NEUTRONS

P. Meijers

Instituut voor Kernphysisch Onderzoek
Ooster Ringdijk 18
Amsterdam, Netherlands

I. Introduction

The fact that the major part of the elements can be determined quantitatively with a sensitivity better than with any other analytical method is the main advantage of activation analysis. Another aspect which can make activation analysis very attractive is the possibility of a nondestructive analysis. For objects of which a partial or total destruction is not permissible, activation analysis, x-ray fluorescence and x-ray diffraction are in general the only methods which can give information about the composition of the object.

As part of the research program of the Institute for Nuclear Physics Research in Amsterdam, several nondestructive activation analysis methods have been developed. They have been applied to objects such as ancient coins (matrix gold, silver or copper), iron meteorites and fossil bones. Irradiation was carried out using the IKO synchrocyclotron (26 MeV deuterons, 30 MeV protons, fast neutrons) and the IKO linear electron accelerator (15-25 MeV photons). This work has recently been published [1].

It will be confined here to a description of the nondestructive determination of copper and silver in gold coins, copper, gold and lead in silver coins and iron, nickel, zinc, arsenic, tin, antimony and lead in copper coins. Irradiation was performed in the extracted beam of the IKO synchrocyclotron. Some information about this cyclotron is given in Table 1. Gold and silver coins were irradiated with 30 MeV protons (obtained by placing a 2.45 g/cm^2 thick copper plate in the 52 MeV proton beam) and 26 MeV deuterons, respectively, copper coins with fast neutrons. Fast neutron irradiation could be achieved by placing a 2.6 mm thick beryllium disc (diameter 15 cm) in the 26 MeV deuteron beam at the end of the beam pipe.

Table 1. Some information on the IKO synchro–cyclotron.

Particles	Max energy (r = 78 cm) MeV	Frequency MHz	Beam current[a] (internal) μA	Beam current (external) nA
Protons	52	21.3 – 19.7	10	35
Deuterons	26	10.65 – 10.25	20	100
$^4He^{++}$	52	10.67 – 10.27	4	not measured
$^3He^{++}$	70	14.4 – 13.6	4	not measured

Magnet : Pole tip diameter = 180 cm
Magnetic field = 1.4 Wb/cm^2

Oscillator: Dee voltage = 16 kV
Repetition rate = 1500 Hz.

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[a] The values given in this column refer to the period 1966–1967. The beam currents have now been improved.

II. Experimental

A. Gold Coins

In order to obtain well defined beam dimensions in the extracted beam, a lead plate (thickness 2 mm) containing several holes was placed in the charged particle beam. Due to a large beam spot (about 50% of the intensity is found within 15 cm^2 and 95% within 60 cm^2), several samples could be irradiated simultaneously. Standard discs of known composition and coins were mounted behind the lead plate. The samples covered the holes completely. They had to be thick enough to stop the charged particles completely. Some charged particle ranges are given in Table 2.

Table 2. Range of 30 MeV protons and 26 MeV deuterons in various metals according to Williamson et al. [2].

Element	Range (g/cm^2) 30 MeV protons	26 MeV deuterons
Copper	1.458	0.685
Silver	1.704	0.823
Gold	2.118	1.061
Lead	2.169	1.089

A thin foil was placed between the lead plate and the samples. The activity of the irradiated parts of the foil is a measure for the charged particle flux. Foils of various materials (copper, gold, silver and stainless steel) can be used for this purpose.

The nuclear reactions of interest are shown in Table 3.

Table 3. Principal nuclear reactions for the determination of copper and silver in gold coins.

30 MeV proton irradiation

Target element	Nuclear reaction	Half life of nuclide produced	Energy of gamma ray used for analysis (keV)
Gold	$^{197}Au(p,pn)^{196}Au$	6.1 d	not used
	$^{197}Au(p,3n)^{195m}Hg$	40 h	not used
	$^{197}Au(p,3n)^{195g}Hg$	9.5 h	not used
	$^{197}Au(n^{a},\gamma)^{198}Au$	2.7 d	not used
Copper	$^{63}Cu(p,pn)^{62}Cu$	9.8 min	511 (annihilation radiation)
	$^{63}Cu(p,n)^{63}Zn$	38 min	
	$^{63}Cu(p,2n)^{62}Zn \xrightarrow{\beta^+} {}^{62}Cu$	9.3 min	
Silver	$^{107}Ag(p,pn)^{106g}Ag$	24 min	not used
	$^{107}Ag(p,pn)^{106m}Ag$	8.3 d	513
	$^{107}Ag(p,p2n)^{105g}Ag$	40 d	not used

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[a] Probably moderated reactor neutrons

The count rate of the 511 keV gamma radiation 20 minutes after the end of the irradiation was determined using a 3 in. × 3 in. NaI(Tl) crystal and a single channel analyzer. The measured count rate mainly due to the activity of ^{62}Cu and ^{63}Zn induced in copper, had to be corrected for the contribution of the ^{106m}Ag and the ^{196}Au activity.

Gamma-ray energy spectra of coins and standard discs were measured using a 8 cm³ Ge(Li) detector about 7 days after irradiation. The activity due to ^{106m}Ag induced in silver was determined using the area of the 513 keV photopeak. A typical gamma-ray spectrum of a gold coin is shown in Figure 1.

B. Silver Coins

Silver coins and standard discs were irradiated during 10 minutes with 26 MeV deuterons as described above. The main nuclear reactions are shown in Table 4.

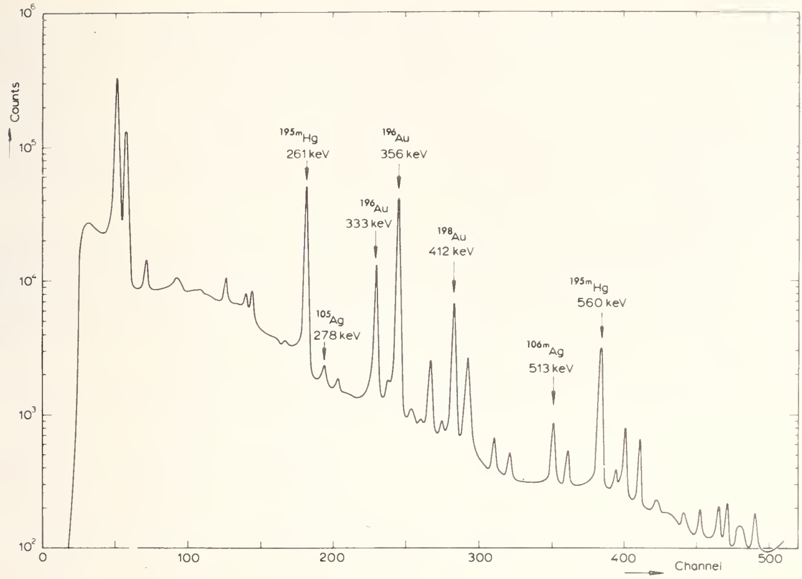

Figure 1. Gamma-ray energy spectrum of a gold coin (Gold Rider No. 1) measured 7 days after a 30 MeV proton irradiation. In this spectrum photopeaks due to ^{196}Au, ^{198}Au, ^{195m}Hg, ^{195g}Hg, ^{106m}Ag and ^{105}Ag can be seen.

Table 4. Principal nuclear reactions for the determination of copper, gold and lead in silver coins.

26 MeV deuteron irradiation

Target element	Nuclear reaction	Half life of nuclide produced	Energy of gamma ray used for analysis (keV)
Silver	^{107}Ag(d,dn)^{106g}Ag	24 min	not used
	^{107}Ag(d,dn)^{106m}Ag	8.3 d	not used
Copper	^{63}Cu(d,2n)^{63}Zn	38 min	511 (annihilation radiation)
	^{63}Cu(d,p)^{64}Cu	12.8 h	511 (annihilation radiation)
Gold	^{197}Au(d,dn)^{196}Au	6.1 d	356
	^{197}Au(d,p)^{198}Au	2.7 d	not used
Lead	^{206}Pb(d,2n)^{206}Bi	6.3 d	184 (343)

The count rate of the 511 keV gamma radiation mainly due to ^{62}Zn, ^{64}Cu and ^{106m}Ag, was determined 3 hours after the end of the irradiation using a 3 in. × 3 in. NaI(Tl) crystal and a single channel analyzer. At that moment the activity induced in copper is of maximal intensity as compared to the activity induced in silver. To obtain the count rate of the activity induced in copper, the contribution of the ^{106m}Ag activity had to be subtracted.

Gamma-ray energy spectra of coins and standard discs were measured 4 or 5 days after irradiation using the Ge(Li) detector. The activity due to ^{196}Au induced in gold and the activity due to ^{206}Bi induced in lead was determined using the areas of the photopeaks at 350 keV and 184 keV, respectively.

A typical gamma-ray spectrum of a silver coin is shown in Figure 2.

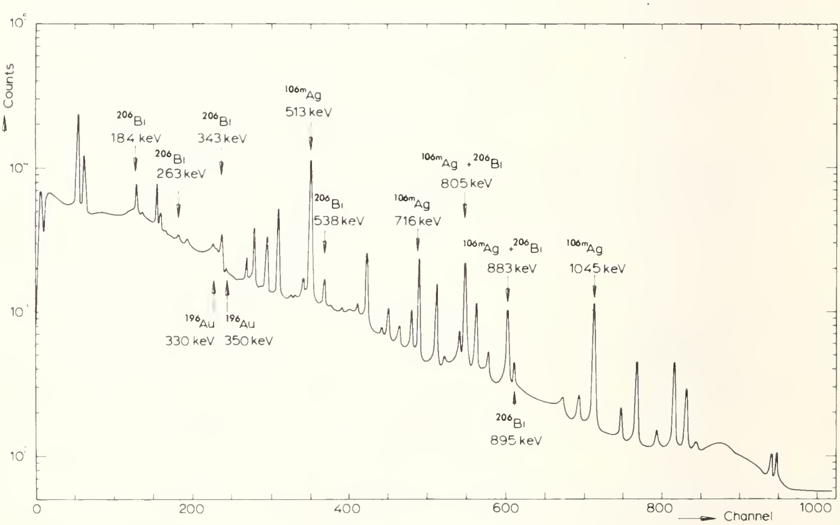

Figure 2. Gamma-ray energy spectrum of a silver coin (No. 43) measured 9 days after a 26 MeV deuteron irradiation. In this spectrum photopeaks of ^{106m}Ag, ^{206}Bi and ^{196}Au can be seen.

C. Copper Coins

For several reasons fast neutron activation analysis of copper coins is preferred to charged particle activation analysis.

As standard samples we used sandwiches of five discs. The numbers 1, 3 and 5 of these sandwiches were copper discs, the numbers 2 and 4 were discs containing the element to be determined. Seven different sandwiches were used in each irradiation, one for each element to be determined.

Coins and sandwiches were irradiated simultaneously for several hours in the fast neutron flux (~2 × 10^{10} n/sec). The main nuclear reactions are shown in Table 5.

Table 5. Principal nuclear reactions for the analysis of objects with a copper matrix.

Target element	Nuclear reaction	Half life of nuclide produced	Energy of gamma ray used for analysis (keV)
Copper	$^{65}Cu(n,2n)^{64}Cu$	12.8 h	511 (annihilation radiation)
	$^{63}Cu(n,\alpha)^{60}Co$	5.3 y	(1173, 1332)
Zinc	$^{67}Zn(n,p)^{67}Cu$	61.1 h	186
	$^{66}Zn(n,2n)^{65}Zn$	245 d	1119
Tin	$^{118}Sn(n,2n)^{117m}Sn$	14 d	159
	$^{117}Sn(n,n')^{117m}Sn$	14 d	159
	$^{112}Sn(n,2n)^{111}Sn \xrightarrow[E.C.]{\beta^+} {}^{111g}In$	2.8 d	not used
Lead	$^{204}Pb(n,2n)^{203}Pb$	52 h	280
Arsenic	$^{75}As(n,2n)^{74}As$	18 d	596
Antimony	$^{121}Sb(n,2n)^{120}Sb$	5.8 d	not used
	$^{123}Sb(n,2n)^{122}Sb$	2.8 d	566
Nickel	$^{58}Ni(n,p)^{58}Co$	71 d	810
Iron	$^{56}Fe(n,p)^{56}Mn$	2.6 h	850 (1870, 2120)

The count rates of the various radioactive products were determined from gamma-ray energy spectra measured at different periods after irradiation using the Ge(Li) detector.

Coins were measured: (1) together with iron discs about 2 hours after irradiation. Photopeaks at 850 keV, 1810 keV and 2120 keV prove the presence of iron. (2) together with copper discs 10-20 hours after irradiation. The photopeak at 511 keV is due to the ^{64}Cu activity induced in copper. (3) together with tin, zinc, antimony, and lead discs, 3-7 days after irradiation. A typical gamma-ray energy spectrum is shown in Figure 3. Activities induced in tin (^{117m}Sn and ^{111g}In), zinc (^{67}Cu),

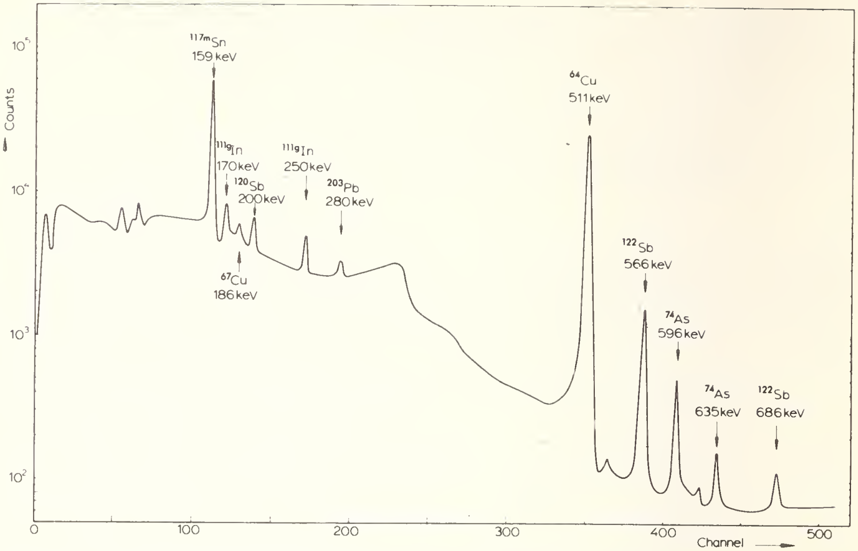

Figure 3. Gamma-ray energy spectrum of a brass coin (No. 27) measured 3 days after irradiation (0-700 keV).

antimony (^{122}Sb) and lead (^{203}Pb) can be observed. (4) together with arsenic, nickel and zinc discs, 7-20 days after irradiation. In the gamma-ray energy spectra one of which is represented in Figure 4, activities

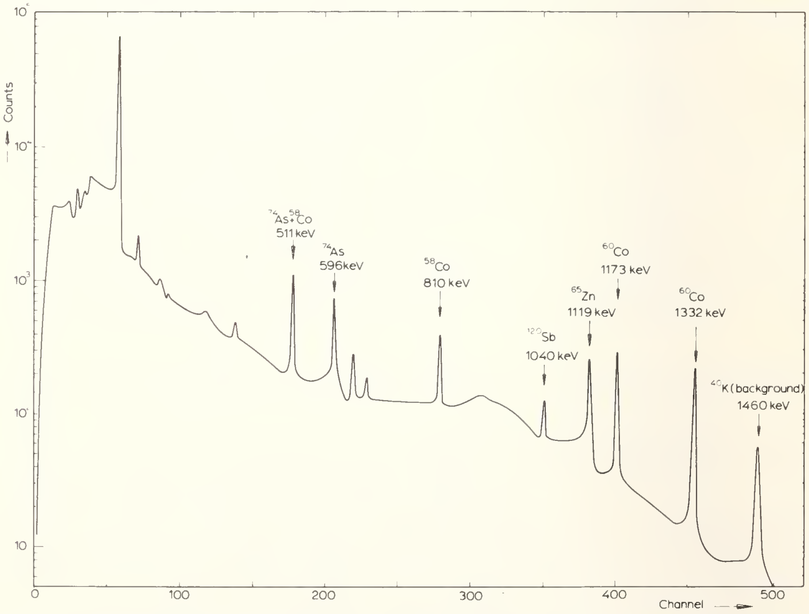

Figure 4. Gamma-ray energy spectrum of a brass coin (No. 27) measured 21 days after irradiation (0-1600 keV).

induced in arsenic (^{74}As), nickel (^{58}Co), Zn (^{65}Zn) and Cu (^{60}Co) can be seen in the energy range 500-1600 keV.

III. Results

A. GOLD AND SILVER COINS

The weight fractions of the elements to be determined in coins were calculated with the formula:

$$W_y = \frac{T_y/F_y}{T_s/F_s} \frac{W_s R_s}{R_y} \tag{1}$$

in which:

W_y = weight fraction to be determined
T_y = count rate of activity of interest in the coin,
T_s = count rate of activity of interest in the standard
F_y = count rate of the piece of foil in front of the coin
F_s = count rate of the piece of foil in front of the standard
W_s = weight fraction of the element of interest in the standard
R_y = range of the charged particles in the coin
R_s = range of the charged particles in the standard.

Equation (1) is based on the work of Ricci and Hahn [3] who derived a simple equation for charged particle activation analysis. Though one could have objections against the rather rigid approximations they made, it proved to be that equation (1) is accurate for our work at least within 3%.

The lower detection limits for copper and silver in gold coins are 0.005 and 0.05% respectively. For copper, gold and lead in silver coins the lower detection limits are 0.01, 0.1 and 0.1%, respectively.

The relative accuracy of the weight fractions varies from 10% up to 50% near the lower detection limits.

Results of the analysis of gold coins are given in Table 6 and of silver coins in Table 7.

B. COPPER COINS

In copper the weight ratio of element X and copper was determined using the equation:

$$P = \frac{T_{1x}}{T_{1y}} \frac{T_{2y}/(W_{2y}G_3)}{T_{2x}/(W_{2x}G_2)} \tag{2}$$

Table 6. Results of the determination of copper and silver in gold coins.[a]

GROUP I. Coins of Roman Republic

No.	mint-master	den.	mint	date B. C.	a.i.	Copper (%)	Silver (%)
1	A. Hirtius	aur.	Rome	46		.05	.74
2	A. Hirtius	aur.	Rome	46		.05	.70
3	L. (Munatius) Plancus	aur.	Rome	45	1	.05	.82
4	L. (Munatius) Plancus	aur.	Rome	45		.05	.75
5	L. (Munatius) Plancus	aur.	Rome	45		.07	1.16
6	C. Numonius Vaala	aur.	Rome	43		.03	.38
7	P. Clodius au	aur.	Rome	41		.10	.13
8	L. Cestius, C. Norbanus	aur.	Rome	44		.06	.30
9	Sextus Pompeius Magnus Pius	aur.	provincial issue	42-38		.15	1.25

GROUP II. Coins of Roman Empire

	Emperor		A. D.			
1	Domitian	aur.	85		.04	.49
2	Domitian	aur.	85		.05	.49
3	Domitian	aur.	85- 86		.02	.14
4	Domitian	aur.	85- 86		.02	.20
5	Domitian	aur.	88- 89		.08	.46
6	Domitian	aur.	81- 84	1	.90	1.1
7	Trajan	aur.	103-111	2	1.6	3.7
8	Trajan	aur.	103-111		.06	.47
9	Trajan	aur.	103-111		.02	.25
10	Trajan	aur.	103-111		.01	.17
11	Trajan	aur.	103-111		.01	.34
12	Trajan	aur.	114-117		.03	1.0
13	Trajan	aur.	114-117		.02	.36
14	Trajan	aur.	114-117		.07	.39
15	Trajan	aur.	115-117	2	1.3	1.8
16	M. Aurelius	aur.	164		.05	.46
17	M. Aurelius	aur.	165-166		.06	.41
18	M. Aurelius	aur.	166		.12	1.3
19	L. Verus	aur.	162-163		.02	.18
20	L. Verus	aur.	163-164		.03	.22
21	L. Verus	aur.	163-164		.03	<.03
22	L. Verus	aur.	163-164		.03	.47

Table 6. Results of the determination of copper and silver in gold coins.[a]
GROUP II. Coins of Roman Empire (continued).

No.	Emperor	den.	mint	date A. D.	a.i.	Copper (%)	Silver (%)
23	L. Verus	aur.		165		.26	.86
24	L. Verus	aur.		165-166		.08	1.2
25	Pertinax	aur.		193		.03	n.m.
26	Pertinax	aur.		193		.20	n.m.
27	Did. Julianus	aur.		193		.33	n.m.
28	Did. Julianus	aur.		193		.09	n.m.
	GROUP III. Coins of late Roman Empire						
1	Valentinian I	sol	Antioch	364-367		.30	5.4
2	Valentinian I	sol	Antioch	364-367		.33	6.0
3	Valens	sol	Antioch	364-367		.23	5.2
4	Valens	sol	Antioch	364-367		.26	5.4
5	Gratian	1½ sc.	Antioch	367-375		.23	n.m.
6	Valens	sol	Antioch	367-375		.10	.78
7	Theodosius I	tr.	Constantinople	383-388		.01	n.m.
	GROUP IV. Coins of India						
1	Kanishka			± 100		.58	.90
2	Kanishka			± 100		.80	.74
3	Kanishka			± 100		.55	.68
4	Kanishka			± 100		.58	1.9
5	Vasu Deva I			± 150		1.04	1.9
6	Vasu Deva I			± 150		.60	1.3
7	Vasu Deva I			± 150		1.09	2.3
8	Vasu Deva I			± 150		.32	.97
9	Vasu Deva I			± 150		.15	1.5
	GROUP V. Coins struck by C. W. Becker (1772 – 1830)						
			ref.				
1	Republic	aur.	Hill 141		early	1.52	4.0
2	Republic	aur.	Hill 144		late	.53	3.7
3	Julia Maesa	aur.	Hill 195		early	.66	1.1
4	Julia Maesa	aur.	Hill 195		late	.22	6.7
5	Julia Mamaea	aur.	Hill 197		early	.80	1.2
6	Julia Mamaea	aur.	Hill 197		late	.36	5.3

Table 6. Results of the determination of copper and silver in gold coins.[a] (continued).

GROUP VI. Coins from province Holland (The Netherlands). A.D. 1750

No.	den.	a.i.	Copper (%)	Silver (%)
1	Gold Rider		3.5	4.3
2	½ Gold Rider		1.6	n.m.
3	Gold Rider	3	<.005	7.4
4	½ Gold Rider	3	<.005	n.m.

Abbreviations used:

den	= denomination	tr.	= triens
a.i.	= additional information	n.m.	= not measured
aur.	= aureus	1	= possible forgery
sol	= solidus	2	= forgery
sc.	= scrupulus	3	= struck by the "Rijks Munt" Utrecht

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[a] All coins were supplied by the "Koninklijk Penningkabinet", The Hague.

in which

$$P = \frac{\text{weight of element X in coin}}{\text{weight of copper in coin}}$$

T_{1x} = count rate of activity induced in element X in coin
T_{1y} = count rate of activity induced in copper in coin
T_{2x} = average count rate of activity induced in element X in discs 2 and 4 of the sandwich
T_{2y} = interpolated average count rate of activity induced in copper in discs 1, 3 and 5 of the same sandwich
W_{2x} = weight fraction of element X in discs 2 and 4 of the sandwich
W_{2y} = weight fraction of copper in discs 1, 3 and 5 of the sandwich
G_2 = average weight of discs 2 and 4
G_3 = average weight of discs 1, 3 and 5.

All count rates were corrected for gamma-ray self-absorption.

Results of the analysis of some Roman orichalcum coins are given in Table 8. (Orichalcum = ancient copper-zinc alloy.) The accuracy of the results varies from 5-20%.

Table 7. Results of the determination of copper, gold and lead in silver coins.[a]

No.	Origin	den.	date B. C.	a.i.	Copper (%)	Gold (%)	Lead (%)
1	Sicily, Naxos.	td.	420-402		3.2	0.70	1.2
2	Sicily, Naxos.	td.	-	1	.05	.23	<.15
3	Macedon, Philip II	td.	359-336		.10	.55	<.15
4	Macedon, Philip II	td.	359-336		.12	1.4	1.0
5	Macedon, Philip II	td.	-	2	.05	.99	1.2
6	Egypt, Ptomely II	ded.	266		.24	.72	.72
7	Egypt, Ptomely II	ded.	250	3	.20	.71	.88
8	Egypt, Ptomely III	ded.	239	3	.20	.35	<.15
9	Egypt, Ptomely III	ded.	223	3	.68	.45	<.10
10	Egypt, Ptomely III	ded.	-	3	2.2	<.14	<.15
		Coins from Bactria					
	King						
11	Antimachos	td.			.30	.24	<.10
12	Eukratides	td.			.37	.24	<.10
13	Eukratides	td.			.04	<.35	1.1
14	Heliokles	td.			6.3	.43	.32
15	Heliokles	td.		4	2.5	<.10	2.1
16	Heliokles	td.		1	1.6	.73	.55
17	Menander	td.		5	2.2	.78	.23
18	Menander	td.			.50	.80	<.15
19	Menander	td.			.70	<.25	.44
20	Menander	td.			.70	<.10	<.15
21	Hippostratos	td.			10.5	.50	2.2
22	Hippostratos	td.			13.5	.43	1.8
23	Hippostratos	td.			14.0	.46	1.1
24	Hippostratos	td.			9.0	.40	1.3

Di- and tetradrachms from Roman Empire.[b]

No.	Origin	Emperor	den.	date A. D.	weight (g)	Cu (%)	Au (%)	Pb (%)	Calc. Ag wt of td.
25	Cyprus	Vespasian	td.	76 - 77	12.71	13.4	.36	1.8	10.7
26	Cyprus	Vespasian	td.	77 - 78	12.37	12.4	.60	1.9	10.5
27	Cyrpus	Vespasian	td.	78 - 79	12.64	12.2	.45	1.9	10.8
28	Cyprus	Vespasian (Titus)	did.	77 - 78	6.315	12.0	.33	1.9	10.8
29	Cyprus	Vespasian (titus	did.	77 - 78	6.31	12.7	.34	n.m.	10.7

Table 7. Results of the determination of copper, gold and lead in silver coins.[a] Di- and tetradrachms from Roman Empire.[b] (continued)

No.	Origin	Emperor	den.	date A. D.	weight (g)	Cu (%)	Au (%)	Pb (%)	Calc. Ag wt of td.
30	Cyprus	Vespasian (Domitian)	did.	77 - 78	6.07	13.7	.39	2.4	10.2
31	Laodicea ad Mare.	Nero	td.	63 - 64	13.46	8.9	.39	.20	12.2
32	Laodicea ad Mare.	Hadrian	td.	122 - 123	13.65	19.0	.61	.24	10.9
33	Antioch	Vespasian	td.	69 - 70	14.95	29.5	.38	.43	10.4
34	Antioch	Vespasian	td.	69 - 70	14.78	27.6	.59	.76	10.5
35	Antioch	Vespasian	td.	71 - 72	14.02	23.5	.53	.68	10.6
36	Antioch	Trajan	td.	103 - 111	15.50	27.5	.13	.90	11.1
37	Antioch	Trajan	td.	109 - 110	13.46	41.0	.35	.75	7.8
38	Antioch	Trajan	td.	110 - 111	14.16	40.3	.31	1.03	8.3
39	Antioch	Trajan	td.	111 - 112	13.67	36.8	n.m.	1.06	8.5
40	Antioch	Trajan	td.	112 - 113	14.21	49.2	.42	.60	7.1
41	Antioch	Trajan	td.	112 - 113	14.26	33.4	.37	.86	9.3

Denarii[b]

No.		Origin	date A. D.	a.i.	Copper (%)	Gold (%)	Lead (%)
42	Balbinus	Rome	238		55.5	.38	.25
43	Balbinus	Rome		1	.05	.52	3.3

Abbreviations used:

den = denomination
a.i. = additional information
td. = tetradrachm
ded. = dekadrachm
did. = didrachm

1 = forgery by C. W. Becker
2 = forgery, 20th century
3 = possible forgery
4 = forgery
5 = the surface of the analyzed part of the coin was contaminated with metallic material

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[a] All coins were supplied by the "Koninklijk Penningkabinet", The Hague.

[b] Data supplied by the "Koninklijk Penningkabinet".

Table 8. Results of the analysis of copper coins.[a]

No.	Emperor	date A. D.	Cu	Zn	Sn	Pb	Ni	As	Sb	Fe
1	Tiberius	35	100	17.6	.21	<.05	.04	<.02	.04	.35
2	Vespasian	71	100	13.4	.24	<.7	.04	.08	.13	<.05
3	Vespasian	71	100	17.5	.06	<.2	.05	.07	.05	.26
4	Titus	80	100	13.6	.04	<.1	.07	.09	.12	.24
5	Titus	80- 81	100	10.0	.72	.1	.04	.03	.10	.24
6	Titus	80- 81	100	12.5	<.03	<.6	.06	<.08	.19	.19
7	Titus	80- 81	100	12.2	.01	.08	.02	.02	.09	.17
8	Titus	80- 81	100	13.9	.02	<.04	.02	.04	.11	.17
9	Titus	80- 81	100	13.2	.06	.15	.02	<.01	.004	.16
10	Titus	80- 81	100	12.7	.20	.10	.04	.02	.11	.30
11	Titus	80- 81	100	13.5	.04	<.07	.03	.04	.08	.29
12	Hadrian	119-121	100	15.8	1.5	.86	.07	.06	.13	.17
13	Hadrian	134-138	100	12.7	.49	1.5	.09	.07	.19	.38
14	Hadrian	117-138	100	12.0	<.01	.22	.07	.07	.15	.27
15	Hadrian	117-138	100	11.8	.01	.19	.09	.05	.17	.20
16	Hadrian	117-138	100	10.0	.46	1.3	.10	.07	.22	.38
17	Hadrian	117-138	100	11.3	1.6	4.4	.39	.18	.21	.95
18	Hadrian	117-138	100	14.9	.18	.35	.10	.06	.14	.32
19	Hadrian	117-138	100	10.2	.02	<.10	.11	.05	.13	.16
20	Hadrian	117-138	100	13.3	.01	.11	.11	.05	.16	.25
21	Antonius Pius	145-146	100	11.5	1.8	<.15	.07	.16	.17	.14
22	M. Aurelius	161-162	100	.40	6.6	8.1	.05	.04	.09	1.1
23	M. Aurelius	162-163	100	7.5	1.1	.27	.07	.12	.24	.52
24	M. Aurelius	162-163	100	7.5	2.1	.12	.06	.10	.21	.49
25	M. Aurelius	163-164	100	6.6	1.1	<.04	.07	.10	.18	.35
26	M. Aurelius	163-164	100	4.5	4.3	<.06	.04	.10	.21	.27
27	M. Aurelius	169-170	100	2.8	3.9	1.2	.06	.14	.24	.24
28	M. Aurelius	171-172	100	4.5	1.4	4.3	.08	.14	.22	.57
29	M. Aurelius	172-173	100	4.4	2.9	.3	.07	.12	.26	.27
30	M. Aurelius	161-	100	7.2	1.9	<.1	.09	.16	.19	.28
31	L. Verus	161-	100	7.9	1.9	<.1	.07	.22	.16	.35
32	M. Aurelius	161-	100	4.4	2.1	<.25	.05	.18	.25	.29
33	M. Aurelius		100	<.15	.01	<.1	.06	.07	.13	.28

Table 8. Results of the analysis of copper coins.[a] (continued)

No.	Emperor	date A. D.	Cu	Zn	Sn	Pb	Ni	As	Sb	Fe
			"Paduan" coins							
34	Caligula		100	13.5	.02	<.3	.02	.09	.08	.28
35	Titus		100	11.8	<.01	.25	.02	.08	.06	.29
36	Caracalla		100	18.9	.06	.75	.11	.09	.02	.23
37	Pertinax		100	5.7	.04	.77	.13	.08	.17	.06
38	Caligula		100	6.5	2.7	1.9	.10	.62	.23	.37

NOTE:

All coins are sestertius except Nos. 33 and 36 which are medallion.

Additional information:

Nos. 17 and 38 – forgery

No. 34 – forgery, probably struck by G. Dal Cavino.

No. 35 – possibly forgery, struck by G. Dal Cavino.

No. 37 – forgery, cast at later date from a forgery by G. Dal Cavino.

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[a] All coins were supplied by the "Koninklijk Penningkabinet", The Hague.

IV. Discussion

On the basis of the composition of the coins, interesting information concerning forgeries, metallurgy, trade relations, *etc.*, has been obtained. The conclusions have been published in detail in ref. [1].

Other nondestructive methods are in general unable to give results of comparable accuracy or sensitivity. X-ray fluorescence can give information only of the surface composition. It is a well-known fact that the composition of the surface of coins may be quite different from the bulk, mainly due to surface enrichment and corrosion. Therefore, x-ray fluorescence is not reliable when bulk analysis is required.

In some cases thermal neutron activation analysis can be applied. In silver coins copper can be determined down to a concentration of 0.01%, gold down to 0.001% [3-5]. In copper coins, traces of gold, silver and antimony have been determined [6-8].

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VI. References

[1] Meijers, P., Thesis, Univ. Amsterdam (1968).

[2] Williamson, C. F., Boujot, J. P., and Picard, J., "Tables of range and stopping power of chemical elements for charged particles of energy 0.05 to 500 MeV", Centre d'Etudes Nucleaires de Saclay, Rapport CEA-R-3042 (1966).

[3] Kraay, C. M., and Emeleus, V. M., "The composition of Greek Silver Coins, Analysis by Neutron Activation". Printed for the visitors and sold at the Ashmolean Museum, Oxford (1962).

[4] Das, H. A., and Zonderhuis, J., Recueil **85**, 837 (1966).

[5] Aitken, M. J., Emeleus, V. M., Hall, E. T., and Kraay, C. M., Neutron activation analysis of ancient silver coins, "Radioisotopes in the Physical Sciences and Industry" **2**, 261, IAEA, Vienna (1962).

[6] Zuber, K., Neutron Activation Analysis of Roman Copper Coins from 250–500 A.D., Part I, Rep. of Cekmece Nucl. Res. Cent. Istanbul, Turkey, T.A.E.C., CNAEM, 21, (1965).

[7] Ravetz, A., Archaeometry **6**, 46 (1963).

[8] Sutherland, C. H. V., Archaeometry **4**, 56 (1961).

THE ANALYSIS OF ENGLISH AND AMERICAN POTTERY OF THE AMERICAN COLONIAL PERIOD[1]

Jacqueline S. Olin [2] **and Edward V. Sayre**

Chemistry Department
Brookhaven National Laboratory
Upton, New York 11973

I. Introduction

Information on the concentrations of elements present in potsherds from a given provenience may be helpful in distinguishing or relating potsherds from archaeological sites. Uniformity of composition has been demonstrated in specimens from various levels of excavation at a given site thus indicating that pottery made at a confined geographic location can be identified by the concentration of some of the elements present.

Pottery sherds found archaeologically in colonial sites serve a multiple purpose. They help to date the sites; they reflect cultural and economic levels in the areas of their use; and they throw light on manufacture, trade, and distribution. An example of this began with the discovery in 1935 of two distinct but unidentified pottery types in the excavations conducted by the National Park Service at Jamestown, Virginia, and later elsewhere along the eastern seaboard.

One type was an elaborate and striking yellow sgraffito ware and the other a coarse utilitarian kitchen ware whose red paste was heavily tempered with a gross water-worn gravel or "grit". For a long time no relationship between them was noted, yet their histories have now been shown to be of the same origin reflecting the activities of a 17th century English pottery-making center of unsuspected magnitude [1].

This study was conducted to determine whether pottery manufactured in North Devon, England, during the 17th century shows a compositional unformity, and whether or not potsherds from American Sites can be distinguished from or identified with the North Devon pottery.

The specimens from North Devon include specimens from two neighboring pottery manufacturing centers, Bideford and Barnstaple. The clay with which the potters worked is reported as having come from three similar deep clay deposits in a valley running parallel with a river called the River Taw and lying between Bideford and Barnstaple [2].

II. Experimental

Samples of approximately 200 mg were analyzed nondestructively by means of neutron activation with gamma-ray spectra measured using a lithium drifted germanium diode detector. The elements determined were scandium, lanthanum, europium, cerium, thorium, chromium, iron and cobalt.

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[1] Research carried out at Brookhaven National Laboratory under contract with the U.S. Atomic Energy Commission.

[2] Research Collaborator from the Smithsonian Institution, Washington, D. C.

A. PREPARATION OF SAMPLES

The samples were cut from the potsherd with a carborundum cutting saw in such a way that a minimum of damage was done to the sherd. They were then leached in distilled water for approximately twenty-four hours in an attempt to remove soluble salts whose concentration might have altered due to past exposure to ground water. The samples were then dried at 100 °C for approximately twenty-four hours.

Finally the samples to be analyzed were cut out to give an approximately square shape in the range of 200 mg and then wrapped individually in aluminum foil.

B. IRRADIATION AND COUNTING

The samples were irradiated in the North 8 irradiation facility of the Brookhaven Graphite Research Reactor for a period of twenty-four hours at a flux of $1.0 \times 10^{13} n \cdot cm^{-2} \cdot sec^{-1}$. Samples of standard glass were irradiated at the same time. All of the elements determined in the pottery are present in measurable concentrations in the glass so that it is possible to monitor each photopeak individually by the corresponding photopeak in the glass.

The samples were counted at four separate times using a 30 cm³ detector for the elements lanthanum, scandium, europium, iron and cobalt and a 12 cm³ detector for cerium, thorium and chromium. Nine days were allowed for the short activities to decay. The samples were then mounted between cellophane adhesive tapes on counting trays made of aluminum and counted.

The counting schedule was as follows:

Element	Detector	Day after activation
Sc	30 cm³	9
La	30	9
Th	12	28–29
Cr	12	28–29
Ce	12	48–49
Eu	30	114–116
Fe	30	114–116
Co	30	114–116

All of the counting data were obtained by direct critical evaluation of the spectra and the calculations were then made using a Wang computer.

II. Results and Discussion

The concentrations are reported as equivalent concentrations of oxides with the following chemical compositions Cr_2O_3, Fe_2O_3, CoO, Sc_2O_3, La_2O_3, CeO_2, Eu_2O_3 and ThO_2. All of these oxides can be considered to be in trace concentrations, *i.e.* in parts per thousand to parts per million, except iron oxide, Fe_2O_3, which is a major component present to about ten percent.

Considered as a whole the North Devon samples divided themselves into two groups according to the concentrations of the elements analyzed. These two groups presented in Tables 1 and 2, are consistent with the two archaeologically distinct groups of North Devon fine ware and North Devon gravel-tempered ware.

Table 1. North Devon fine ware, concentration in percent of oxide.

Analytical specimen No.	Scandium Sc_2O_3	Lanthanum La_2O_3	Europium Eu_2O_3	Cerium CeO_2	Thorium ThO_2	Chromium Cr_2O_3	Iron Fe_2O_3	Cobalt CoO
1	.0024	.0046	.000157	.0097	.00085	.0110	9.6	.00228
2	.0023	.0047	.000142	.0099	.00087	.0069	8.8	.00215
3	.0026	.0052	.000163	.0091	.00069	.0092	10.3	.00240
4	.0024	.0052	.000169	.0096	.00073	.0103	10.3	.00264
5	.0027	.0048	.000164	.0097	.00061	.0104	10.6	.00245
6	.0023	.0050	.000155	.0091	.00066	.0078	9.4	.00229
7	.0028	.0056	.000176	.0104	.00110	.0141	10.6	.00265
Mean of group	.0025	.0050	.000161	.0096	.00077	.0097	9.9	.00240
Standard deviation as percent of mean	8.2	7.1	7.1	4.8	22.0	26.5	7.5	8.1

A comparison of the mean concentration of the two groups which is given at the bottom of Table 2, shows that the concentrations of these elements in North Devon gravel ware are uniformly approximately 85 percent of those in the North Devon fine ware. It is as if the North Devon gravel ware had been diluted with a material which was relatively free of the elements that have been determined. Since it is recognized that the fine ware is essentially free of an additive temper while the coarse ware has had sand added to it, it seems very probable that the sand has acted as a relatively pure diluent and that the concentration levels of these trace impurities in both wares, primarily are determined by the clay.

Table 2. North Devon gravel ware, concentration in percent of oxide.

Analytical specimen No.	Scandium Sc_2O_3	Lanthanum La_2O_3	Europium Eu_2O_3	Cerium CeO_2	Thorium ThO_2	Chromium Cr_2O_3	Iron Fe_2O_3	Cobalt CoO
8	.0021	.0039	.000124	.0075	.00083	.0082	10.7	.00187
9	.0022	.0046	.000147	.0095	.00065	.0100	9.2	.00214
17	.0018	.0046	.000116	.0069	.00056	.0077	7.8	.00198
Mean of group	.0020	.0044	.000128	.0079	.00067	.0086	9.2	.00199
Standard deviation as percent of mean	11.1	10.0	13.0	18.0	22.0	14.6	17.2	7.0
Ratio of gravel–ware mean to fine–ware mean	.80	.88	.80	.82	.87	.89	.92	.83
average ratio	.85							

The mean value for each element of the North Devon specimens has been calculated as a geometric mean. This is based on evidence that in a group of specimens of a given provenience, the deviation from the mean concentration value is of a fractional rather than an absolute amount. This fractional variation has been shown to be about the same percentage of the mean concentration whether one is considering a major component or a trace impurity.

Table 3 contains the analytical data on pottery sherds similar in style and construction to the North Devon ware but found at American sites. To estimate the probability of English or American manufacture of these specimens, a statistical comparison between them and the known North

Table 3. Miscellaneous sherds from American sites, concentration in percent of oxide.

Fine–Ware

Analytical specimen No.	Site	Scandium Sc_2O_3	Lanthanum La_2O_3	Europium Eu_2O_3	Cerium CeO_2	Thorium ThO_2	Chromium Cr_2O_3	Iron Fe_2O_3	Cobalt CoO
13	Jamestown	.0026	.0054	.000162	.0084	.00074	.0121	8.1	.00238
14	Kent Island, Md.	.0027	.0053	.000167	.0100	.00110	.0135	8.7	.00235
19	Pemaquid, Maine	.0024	.0052	.000160	.0065	.00059	.0088	10.4	.00255
20	Jamestown	.0028	.0049	.000137	.0080	.00049	.0161	10.9	.00192

Gravel–Ware

Analytical specimen No.	Site	Scandium Sc_2O_3	Lanthanum La_2O_3	Europium Eu_2O_3	Cerium CeO_2	Thorium ThO_2	Chromium Cr_2O_3	Iron Fe_2O_3	Cobalt CoO
10	Jamestown	.0023	.0043	.000143	.0089	.00103	.0099	8.6	.00201
11	Angelica Knoll, Md.	.0022	.0040	.000135	.0072	.00069	.0098	8.4	.00204
12	Plymouth, Mass.	.0019	.0037	.000119	.0064	.00067	.0065	7.4	.00172
18	Pemaquid, Maine	.0023	.0053	.000140	.0087	.00079	.0093	9.0	.00226
15	Drake's Bay, Calif.	.0024	.0030	.000120	.0061	.00081	.0013	11.2	.00240
16	Drake's Bay, Calif.	.0019	.0044	.000102	.0093	.00112	.0072	4.9	.00167
27	Bayley Kiln Site Newberry Port, Mass.	.0020	.0059	.000172	.0104	.00093	.0088	9.0	.00210

Devon specimens was made. Since the possibility of uniform dilution through addition of temper exists, this comparison was made on an absolute and a best relative fit basis. Student's statistics for small populations was employed to compensate for the fact that only a limited number of specimens was available to us. The result of this comparison reveals that although most of these specimens from American sites agree in composition with those from North Devon and in all probability were imported from there, several of them, particularly the two from Drake's Bay, California, show significant compositional differences from them in several elements.

III. Acknowledgment

We wish to thank C. Malcolm Watkins of the Museum of History and Technology, the Smithsonian Institution, for his generosity in providing the specimens for analysis and his encouragement of our study.

IV. References

[1] Watkins, C. M., United States National Museum Bulletin **225,** 17 (1960).
[2] Maw, G., Quarterly Journal of the Geological Society of London **20,** 445 (1864).

COMPARISON OF FORENSIC SOIL SPECIMENS BY NEUTRON ACTIVATION ANALYSIS

C. M. Hoffman, R. L. Brunelle, K. B. Snow and M. J. Pro

Alcohol and Tobacco Tax Division
Internal Revenue Service
Washington, D. C. 20224

I. Introduction

Laboratories engaged in the examination of physical evidence are frequently required to determine whether questioned and known soil specimens come from the same location. Currently, this comparison is carried out by the density gradient and microscopic methods [1]. While much information can be obtained about the comparative physical properties of soils by these methods, similarity between the samples depends primarily upon proper sample selection by the investigating officer. It is well known that considerable physical variations can occur between soils taken only a few feet apart, and questioned and known samples from the same general location may appear different when examined by these methods.

In most criminal examinations it is only necessary to establish that questioned and known soils come from the same localized area. The development of a method and the assessment of a technique for accomplishing this would therefore be desirable. It was felt that the trace elemental distribution of this material, as determined by neutron activation analysis (NAA), might provide the basis of these trace elemental differences, a study was made of the elemental distribution in soils selected from three areas of the United States. An evaluation of these data was also made to determine the individuality of soils having a particular elemental composition. This work was supplemented by atomic absorption analysis which was used to measure the major constituents and those trace elements not particularly amenable to nondestructive neutron activation analysis.

II. Experimental

A. Apparatus

All of the soil samples were irradiated in a thermal neutron flux of approximately 7 × $10^{12} n \cdot cm^{-2} \cdot sec^{-1}$. The gamma-ray spectra were obtained with an RIDL 34-12B 400 channel analyzer using a 3 in. × 3 in. NaI(Tl) detector housed in a large volume mercury filled shield. The readout equipment consisted of Mosley X-Y plotter and Hewlett-Packard Printer.

B. PROCEDURE

Samples were collected from flat fields located in the states of Georgia, Texas and Washington, as indicated in the collection patter shown in Figure 1. Flat areas were chosen to minimize differences in composition and only surface soils of less than 1/2 in. depth were taken since this type of specimens is most frequently encountered in criminal investigations.

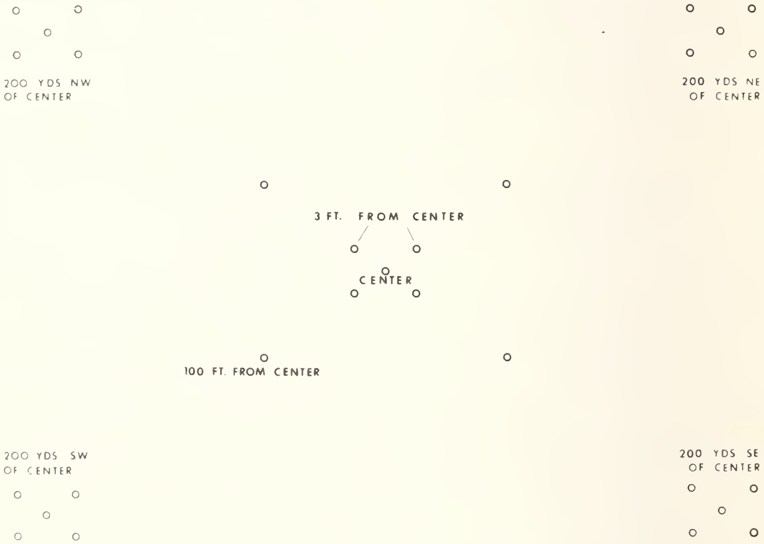

Figure 1. Soil collection grid. Collection points indicated by o.

Each sample was first passed through a 60 mesh sieve to remove stones and plant material, and a 500-mg portion of the 60-mesh fraction was placed in a small vial and heat sealed. The samples from each grid location were simultaneously irradiated for 10 minutes and subsequently transferred to nonirradiated polyvials prior to counting. The samples were counted 1 hour after irradiation and again at decay times of 1, 3, 7 and 14 days.

Variations in the neutron flux were monitored with copper standards and the elements in the specimens were quantitated by a modified comparator technique. Peak areas were calculated using Covell's method [2].

The precision of the neutron activation analysis measurement was determined by selecting one sample from each collection grid and analyzing each of these samples in triplicate. The precision for the elements quantitated is shown in Table 1.

Table 1. Nondestructive NAA precision study.

Element	Precision (%)
Chlorine	± 30
Manganese	± 5.5
Sodium	± 15
Scandium	± 5.2
Barium	± 9.6
Lanthanum	± 14.2
Samarium	± 3.2

III. Results and Discussion

A. Results

The distribution of elemental concentrations over the 400 yd. diameter collection grid varied for some of the elements while others were much more uniform. In Figure 2, the manganese distribution illustrates concentration differences observed over the Dallas collection grid.

To assess concentration variations for a given element, the concentration range of each element was divided into analytically distinguishable increments. Each increment was calculated on the basis of three times the analytical precision for the element multiplied by the average concentration of that element in appropriate collection grid. For example, the average manganese value in the Georgia grid is 620 parts per million (ppm) with an analytical precision of ±5.5%. Then: (3) (±5.5%) = 16%; and: (620 ppm) (±0.16) = 620 ±100 ppm; or: A range of 520 ppm to 720 ppm. The distribution of elements in the soil from the Georgia collection grid, is shown in Table 2. The analytically distinguishable increments calculated as described above are indicated in the ppm range column of this table.

Using this approach it is possible to estimate the individuality of a soil from a particular location which has a specific trace elemental composition. The individual elemental probability of occurrence for a specific concentration range is equal to the number of samples in that range divided by the total number of samples measured. The total probability of finding a soil containing manganese, samarium, *etc.* in specific ranges is the product of the individual probilities for these

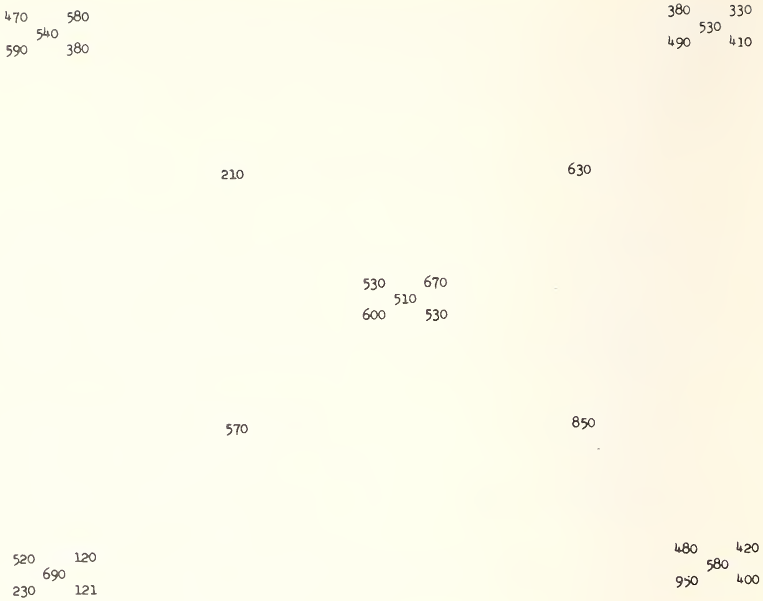

Figure 2. Manganese distribution in Dallas collection grid.

elements. Soils from different locations can be easily individualized and distinguished by both qualitative and gross quantitative differences in composition.

In the three areas a total of 11 elements were measured by neutron activation analysis: samarium, lanthanum, barium, chlorine, protactinum, cesium, hafnium, scandium, sodium, chromium and cerium. An additional 10 elements (K, Al, Sr, Mg, Li, Rb, Ca, Ni, Cu, and Zn) were measured by atomic absorption analysis in these soil samples.

B. Discussion

The sample grids were selected to represent reasonably large localized areas. It was shown that soils taken within a 100 ft. radius are similar in trace elemental composition but that qualitative and quantitative variations become significant as this radius is increased. This work indicates that the measurement of the trace elemental composition provides valuable information in the comparison of soils, and it provides information based on non-physical properties of the material.

Using NAA, it is possible to measure approximately 10 elements nondestructively. When quantitated, the presence of these elements provide the points of comparison necessary in comparing two or more soil samples.

Table 2. Concentration ranges for elements in Georgia grid.

Range (ppm)	Number of samples	Range (ppm)	Number of samples
Samarium		Manganese	
0–8	8	43–247	5
9–25	5	248–352	0
26–42	6	353–557	9
43–59	5	558–762	5
60–76	4	763–967	0
77–93	0	967–1170	4
94–110	0	1171–1380	5
111–127	0	1381–1580	1
128–144	0		
145–161	0	Lanthanum	
162–178	1	0–133	17
		134–400	11
Scandium		401–667	1
0.12	18		
13–25	6	Sodium	
25–37	4	0–320	6
38–50	0	321–741	17
51–62	0	742–1160	6
63–75	1		

If AA is also used in the examination of the soil samples an additional 10 elements can be measured, increasing the number of points to 20. With this large number of elements, the relative origin of soil samples can easily be established.

IV. References

[1] Nickolls, L. C., Methods of Forensic Science, F. Lundquist, Ed., Interscience, New York, Vol. 1., 1962, pp. 355-62.

[2] Covell, D. F., Anal. Chem. **31**, 1965 (1959).

RECENT FORENSIC APPLICATIONS OF INSTRUMENTAL ACTIVATION ANALYSIS

Auseklis K. Perkons

The Centre of Forensic Sciences
8 Jarvis Street
Toronto 2, Ontario

Robert E. Jervis

Department of Chemical Engineering and Applied Chemistry
University of Toronto
Toronto 5, Ontario

I. Introduction

The development and introduction of high resolution solid state radiation detector systems in the field of activation analysis during the last few years [1,2] has resulted in significant advances in the use of nondestructive trace characterization of evidence materials involved in forensic investigations [3]. The enhanced resolution of the detectors has enabled the forensic scientist to measure a sufficient number of significant trace characteristics in a small sample to be able to individualize similar exhibits, determine the origin or history of questioned exhibits, or identify traces of foreign substances in various materials without having to resort to lengthy and destructive radiochemical separation procedures of sophisticated techniques of gamma-ray spectrum analysis [4,5].

This paper lists some of the recent advances in forensic activation analysis (FAA) and presents data proving the feasibility of improved forensic applications of the technique in a variety of investigations.

II. Procedure and Instrumentation

Small amounts of the evidence material, *e.g.*, a small bundle of hair or single hairs, small chips of bone, a few mg of skin tissue or narcotic drug are carefully sealed in polyethylene tubing together with suitable standards, packaged in aluminum containers, and irradiated in a 1 to 2 × 10^{13}n·cm^{-2}·sec^{-1} thermal neutron flux for 1 to 40 hours depending upon the activation cross sections and decay half lives of the constituent isotopes under investigation.

After irradiation and appropriate decay periods, the samples are removed for the polyethylene vials and counted. The two detector systems in use at the Toronto Centre of Forensic Sciences are a Harshaw 3 in. × 3 in. NaI thallium activated scintillation crystal, and a 30 cm^3 coaxial premium resolution Ge(Li) detector, both coupled through suitable high performance amplifier systems to a 400 channel pulse-height analyzer. The Ge(Li) detector system gives overall resolution values of 3.5 keV (FWHM of the 1.33 MeV ^{60}Co photopeak) as compared to the 90 keV value for the NaI crystal. Moreover, the 12:1 photopeak-to-Compton ratio of the Ge(Li) detector compares very favorably with the 5:1 ratio of the NaI scintillator.

Figure 1 serves to illustrate the improvement in the photopeak resolution of a gamma-ray spectrum available by use of the Ge(Li) as

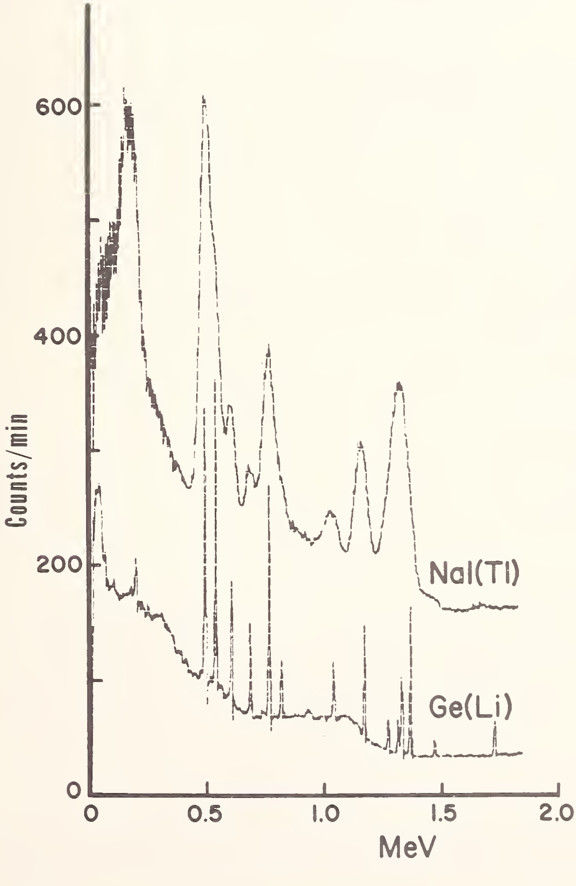

Figure 1. Comparison of NaI and Ge(Li) gamma-ray spectra of hair.

compared to the NaI crystal in the instrumental analysis of a representative hair sample.

III. Results and Discussion

A. HAIR ANALYSES

The individualization of human head hair by instrumental neutron activation analysis (NAA) is one of the most important forensic applications of the technique [6-8]. Use of the Ge(Li) detector in a comparison study of 20 hair samples resulted in the identification of 24 different nuclides in the hair. The nuclides are listed in Table 1. Using the NaI counter, only those 9 nuclides marked with an "a" were identified in the spectra. Thus it is evident that a much improved probability of individualization is associated with the use of a high resolution Ge(Li) system and a doubtful match of two hair samples may be rendered a virtually certain match by merely improving the resolution of the detector.

Table 1. Trace components in 20 human hair specimens.

^{24}Na [a]	^{65}Zn [a]	^{122}Sb [a]
^{46}Sc	^{72}Ga	^{124}Sb [a]
^{51}Cr	^{76}As	^{134}Cs
^{54}Mn (from Fe)	^{75}Se [a]	^{140}La
^{56}Mn	^{82}Br [a]	^{141}Ce
^{58}Co (from Ni)	^{86}Rb	^{198}Au [a]
^{60}Co	^{87m}Sr	^{197m}Hg
^{64}Cu [a]	^{110m}Ag	^{203}Hg [a]

[a] See text.

Similar results were obtained from the analyses of hair samples from four Northern Ontario wolves. Figures 2 to 4 show comparison of the amounts of six constituent elements measured both by the NaI and Ge detectors. The overlap of the statistical errors makes differentiation of the four wolves from the NaI analyses practically impossible, whereas the Ge(Li) results show that individualization can be achieved. In addition, five more constituents were detected using the Ge(Li) system (Fig. 5), four of them, with exception of potassium, providing additional characteristic differences among the hair samples.

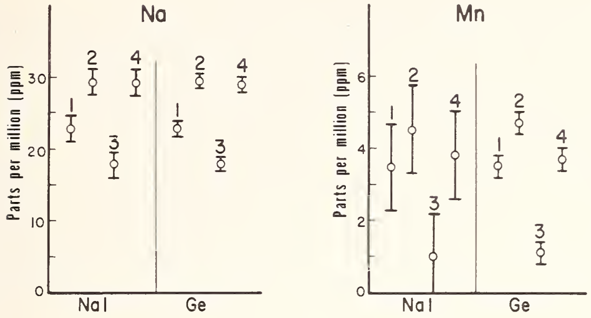

Figure 2. Trace element concentration of wolf hair—Na and Mn.

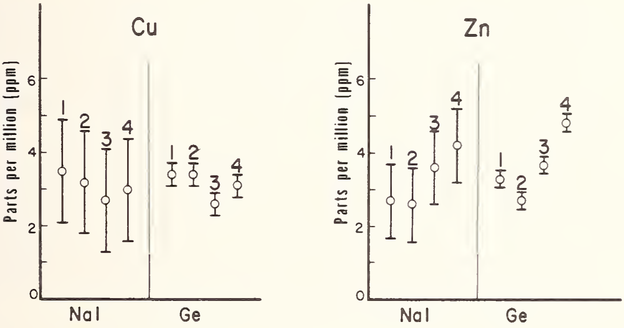

Figure 3. Trace element concentration of wolf hair—Cu and Zn.

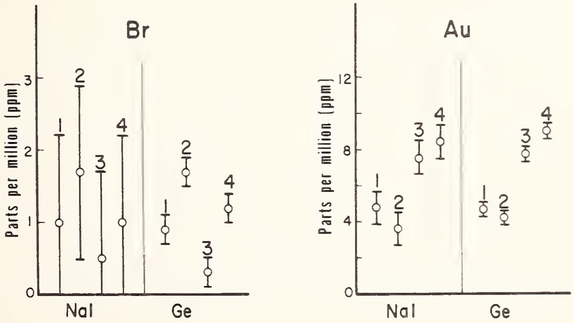

Figure 4. Trace element concentration of wolf hair—Br and Au.

B. ELECTROCUTION

In cases of sudden death in connection with possible electrical shock and its accompanying cardiac arrest it is sometimes very difficult to determine the immediate cause of death. The deceased may have had a

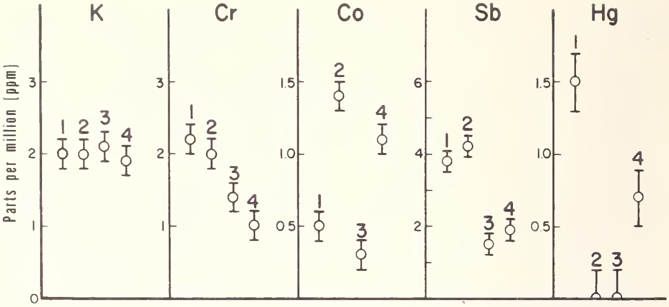

Figure 5. Trace element concentration of wolf hair—K, Cr, Co, Sb and Hg.

bad heart condition, and any localized burns in evidence may not be readily apparent as being electrical burns, but may have thermal or chemical origins. In such cases trace analysis can be used to detect the trace deposition of vaporized metals on skin resulting from a lethal electrical discharge [9].

Figure 6 shows bar diagrams of the copper and sodium contents determined by NAA in five skin samples of burns, compared to four samples of uninjured skin from the hands of a victim known to have been in contact with high voltage copper conduits. The copper deposition on the burned portions is immediately apparent.

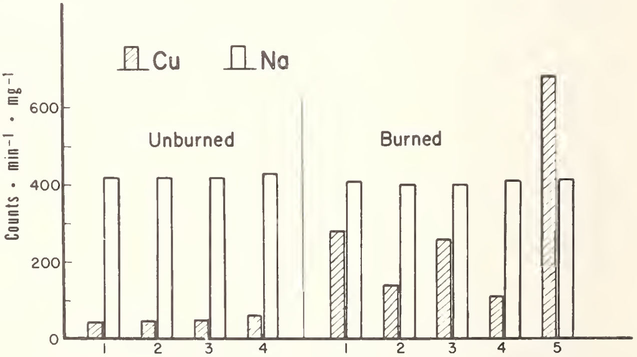

Figure 6. Copper and sodium activities of irradiated skin specimens.

Another case involved an electrical maintenance worker found dead near electrical equipment. The victim had a history of slight heart irregularities, but had also minor burns on his hands, although all power to the equipment was supposedly terminated. Analysis of skin samples from the burned locations revealed the presence of trace amounts of iron and cadmium, as depicted in Figure 7. Further investigation revealed that an air nozzle used by the victim at the time of his demise had an iron—cadmium alloy shut-off valve, indicating a probable connection with the NAA findings. Thus, FAA can be used not only to identify an electrical burn, but also to characterize the particular conductor involved.

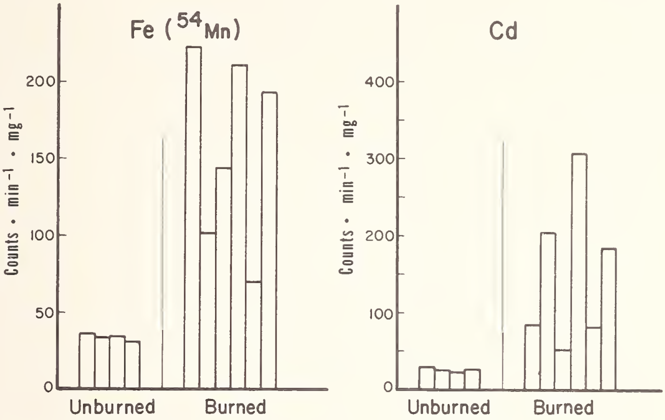

Figure 7. Iron and cadmium activities of irradiated skin specimens.

C. Bullet Residue on Bone

A very simple and elegant application of FAA was devised for the identification of bone fractures caused by lead bullets. The presence of lead deposits on bone is indicated by the activity of ^{122}Sb and ^{124}Sb resulting from irradiation of the antimony alloyed with lead in bullets to give it the required hardness. Three tests on human skulls were performed, using 22 calibre lead bullets (Table 2). Test 4 gives results of the analysis of a damaged skull which had been buried for over 20 years.

It is evident that the antimony (and hence lead) concentration falls rapidly with distance from the bullet hole, and is not present in detectable amounts in clean bone. The relatively high amounts of antimony around the fracture identified it irrefutably as a bullet hole. This pattern is still present after considerable mistreatment of the bone, *e.g.*, test 4 in which case the lead has probably oxidized and diffused further than in a fresh fracture, but which nonetheless signals that the bone has been in contact with material containing antimony, such as lead bullet alloy.

D. Narcotic Drugs

The origin of narcotic drugs can also be indicated by FAA of their characteristic trace constituents [3,10]. Table 3 gives the results of analysis of 30 opium samples from over 20 different locations of the

Table 2. Antimony concentrations (ppm) in bone chips.

Sampling location	Test 1.	Test 2.	Test 3.	Test 4.
Side of entry hole:	376	207	286	–
"	125	275	377	–
"	–	–	158	–
"	–	–	168	–
"	–	–	151	–
Side of exit hole:	44	7	26	24
"	75	13	26	27
"	–	–	10	30
"	–	–	58	–
"	–	–	8	–
½ in. to 1 ½ in. from exit hole	68	2	8	10
"	2	0.5	1	–
"	16	–	2	–
"	6	–	0.5	–
"	–	–	0.5	–
Over 3 in. from exit hole	nil	nil	nil	4
"	–	–	–	3
"	–	–	–	8
Bone chip imbedded in bullet	279	–	399	–

world. Samples marked 1, 2 and 3 originate from the same region, whereas samples marked A and B come from different regions or states of the same country. It is interesting to note that the presence of some elements (Ag, Sb, Au, Mn, Cr, As) and the absence of others (Sc, Fe, Cu, Zn, Br) can serve to suggest the country or origin. Similar origin studies can be performed by FAA on other natural or synthetic narcotic substances.

IV. Conclusion

Instrumental activation procedures are being applied to a wide variety of evidence materials which are encountered in the investigation of crime. Not only is gamma spectrometry more readily applied as a routine technique in the crime laboratory than radiochemical procedures, but the analyses can be repeated as required, and the results are often in a form more suitable for presentation as evidence in court. The activation method allows investigations that were hitherto not possible by other analytical procedures employed in police laboratories and hence should find increasing use in forensic investigations.

Table 3. Trace constituents in opium (ppm).

Country of origin	Na	K	Sc	Fe	Cu	Zn	Br	Ag	Sb	Au	Mn	Cr	As
Algeria	1230	3,215	–	70.9	405	180	15.8	–	–	–	–	–	.65
Burma	485	2,332	.022	5.8	448	312	45.0	–	19.0	–	–	–	–
Cambodia	1318	8,830	.038	–	30	16	43.3	–	–	–	–	–	–
China 1	440	3,844	.030	24.4	660	1	17.5	–	.6	–	–	–	–
China 2	551	4,810	.024	29.3	786	1	2.1	–	–	–	–	–	–
Greece A	989	10,080	.026	35.5	104	251	–	–	–	1.40	11.65	–	–
Greece B	745	8,630	.043	28.0	118	14	–	–	5.8	–	9.17	.50	–
India A	244	12,300	.092	82.3	34	–	10.9	–	–	–	–	–	–
India B	70	20,600	.017	75.6	339	44	2.9	–	–	–	–	–	–
Indonesia A	1015	12,600	.080	28.0	38	198	–	3.2	–	–	–	–	–
Indonesia B	744	9,400	–	53.7	22	–	–	–	7.5	–	15.40	–	–
Iran	495	1,855	.060	22.8	548	2	–	–	–	1.64	–	–	–
Iraq 1	1654	4,550	.160	17.3	188	15	–	33.6	–	–	3.22	–	–
Iraq 2	1602	4,935	.185	48.9	169	64	–	19.6	–	–	5.18	–	–
Israel	644	6,620	–	63.0	93	19	34.0	–	–	.44	–	–	–
Japan	93	8,200	–	–	28	152	–	–	26.4	–	–	–	–
Korea	1065	6,504	–	6.9	507	22	118.4	–	–	.86	4.18	–	–
Laos A	186	960	.013	–	20	4	84.9	–	–	–	–	–	–
Laos B	868	16,380	–	–	106	11	86.0	–	13.4	–	–	–	–
Lebanon	409	12,000	–	35.4	98	35	9.2	2.3	–	–	.84	–	–
Libya	69	1,808	–	38.6	49	53	13.8	.7	–	–	–	1.16	2.27
Morocco	140	3,060	.108	–	76	59	–	76.9	–	–	1.77	–	–
Pakistan	643	9,760	.307	16.0	279	–	8.8	14.0	–	–	–	–	–
Philippines	108	19,680	–	49.0	39	60	38.4	1.8	–	–	–	–	–
Thailand	127	4,030	–	–	316	103	6.6	–	–	–	–	–	–
Tunisia	360	5,000	.075	90.4	17	43	2.4	–	.5	–	6.13	–	.10
Turkey 1	283	2,615	.038	118.0	9	79	58.3	–	–	.05	–	2.28	–
Turkey 2	305	2,580	.030	98.5	11	79	16.8	–	–	–	–	2.40	–
Turkey 3	289	2,265	.039	104.0	11	84	48.0	–	.4	.02	–	2.09	–
Yugoslavia	167	14,600	.027	80.5	–	442	5.2	–	10.4	–	–	–	–

Further details of these and other applications of activation analysis techniques are outlined in a new monograph [11].

V. References

[1] Girardi, F., Guzzi, G., Pauly, J., Radiochimica Acta **6**, 202 (1967).

[2] Camp. D. C., U.C.R.L. Rept. #50156 (March 1967).

[3] Perkons, A. K., Jervis, R. E., Proc. 1st National Symposium on Law Enforcement Science and Technology, Chicago, March 1967, pp. 257-266.

[4] Perkons, A. K., Jervis, R. E., Trans. 14th Annual Meeting of the ANS/CNA, Toronto, June 1968, pp. 82-83.

[5] Krishnan, S. S., Perkons, A. K., Erickson, N. E., Trans. 14 Annual Meeting of the ANS/CNA, Toronto, June 1968, p. 79.

[6] Perkons, A. K., Proc. 1st International Conference on Forensic Activation Analysis, San Diego, Calif., Sept. 1966, pp. 221-235.

[7] Jervis, R. E., Perkons, A. K., Mackintosh, W. D., Kerr, M. F., Proc. 1961 International Conf. on Modern Trends in Activation Analysis, College Station, Texas, Dec. 1961, pp. 107-113.

[8] Perkons, A. K., Jervis, R. E., Proc. 1965 International Conf. on Modern Trends in Activation Analysis, College Station, Texas, April 1965, pp. 295-303.

[9] Bohm, E., Dtsch. Z. Ges. Gerichtl. Med. **59,** 26-34 (1967).

[10] Rayudu, G. V. S., Tiefenbach, B., Jervis, R. E., Trans. 14th Annual Meeting of the ANS/CNA, Toronto, June 1968, pp. 81-82.

[11] Jervis, R. E., Perkons, A. K., Krishnan, S. S., "Nuclear Methods in Crime Detection", University of Toronto Press (in press).

THE EXAMINATION OF ACTUAL CASE EVIDENCE SAMPLES BY NEUTRON ACTIVATION ANALYSIS

H. L. Schlesinger, H. R. Lukens, and D. M. Settle[1]

Gulf General Atomic Incorporated
San Diego, California

I. Introduction

Starting about 1½ years after the inception of forensic activation analysis research at this laboratory in 1961, effort has also been devoted to the examination of actual evidence samples, whenever it was believed that information relevant to the investigating agency could be obtained. The present paper summarizes some of this case work in the areas of hair analysis, detection of gunshot residues, bullet lead analysis, paint analysis for the purpose of art work authentication, and detection of mercury in a case of alleged animal poisoning. In particular, cases of some special interest or importance were selected for inclusion.

Discussion of actual cases in which neutron activation analysis (NAA) has been employed are rare in the literature. It is hoped that this paper will be useful both to groups interested in doing work in this field, and to groups presently engaged in such work.

II. Experimental

A. Hair Analysis Case

A considerable body of work exists [1-4] that is concerned with the problem of characterizing hair by means of high flux instrumental NAA. A major problem is the one of washing the hair to remove surface contamination, but without altering the trace-element content. The analysis itself is relatively routine.

The case illustrated in Table 1 involves human head hair removed from a suspect's car (the Q samples) and head hair from a murder victim (the K samples). The Q samples ranged from 7 to 17 cm in length. Each Q sample was compared with a K sample of equal length. The irradiations were performed in the Gulf General Atomic Mark I TRIGA nuclear reactor. The irradiation time was 125 minutes. A longer irradiation was ruled out by a court order requiring that the hairs be physically unaltered by the analytical procedure [5]. The results are shown in Table 1, and are discussed below.

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[1] Presently affiliated with the California Institute of Technology, Pasadena, California.

Table 1. Analytical results from NAA of some hair samples in a murder case.

	Sample weight	ppm of element found[a,b]						
Sample	(μg)	Iodine	Copper	Manganese	Zinc	Sodium	Chlorine	Bromine
K−3	699	1080 ± 70	< 1	17 ± 1	200 ± 100	760 ± 40	2400 ± 200	32 ± 6
K−4	482	< 40	34 ± 4	27 ± 1	600 ± 200	105 ± 8	120 ± 30	17 ± 5
K−6	420	670 ± 60	3 ± 4	28 ± 2	1300 ± 300	680 ± 40	650 ± 70	46 ± 9
K−7	404	240 ± 40	14 ± 5	28 ± 1	300 ± 200	600 ± 30	1000 ± 100	43 ± 8
K−8	418	< 130	21 ± 4	19 ± 1	1400 ± 300	220 ± 20	140 ± 50	17 ± 6
K−9	373	< 180	11 ± 3	29 ± 2	1100 ± 300	290 ± 20	380 ± 80	22 ± 6
K−11	375	< 660	8 ± 3	5.8 ± 0.4	< 540	1140 ± 60	2400 ± 300	27 ± 8
K−12	233	< 700	10 ± 2	24 ± 1	1100 ± 300	180 ± 10	200 ± 200	17 ± 7
Q−3	504	< 29	68 ± 6	0.7 ± 0.2	< 270	420 ± 20	780 ± 50	< 7.3
Q−4	343	< 39	48 ± 4	0.5 ± 0.2	< 310	300 ± 20	830 ± 60	< 7.8
Q−6	244	< 89	37 ± 4	1.4 ± 0.3	< 560	580 ± 40	1400 ± 100	22 ± 8
Q−7	241	< 68	29 ± 2	0.5 ± 0.1	< 430	160 ± 10	530 ± 50	< 9.2
Q−8	325	< 100	37 ± 2	0.28 ± 0.08	< 360	140 ± 10	690 ± 60	< 8.0
Q−9	428	< 170	44 ± 2	0.3 ± 0.1	< 340	440 ± 30	930 ± 90	< 7.4
Q−11	402	< 1000	29 ± 2	< 0.26	< 420	610 ± 30	1200 ± 300	< 9.4
Q−12	360	< 1100	28 ± 2	< 0.28	< 440	680 ± 40	1700 ± 300	< 9.3

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[a] The plus–or–minus values shown represent one standard deviation (1σ) of the value, computed only from counting statistics.

[b] The value shown following the < sign is a 3σ upper limit, i.e., the greatest concentration of the element that could be present but still escape detection (where none could be detected).

A surprising fact is that there was found to be considerably more uniformity in the trace-element composition of hairs found in the car than in those from the victim. A ranking test, where elemental concentration was compared with hair length, showed no significant correlation between length and composition. The K samples were treated as a homogeneous group; means and standard deviations were computed for all elements detected except iodine. This information is shown in Table 2. No manganese level found in the Q samples is within the range of values for that element found in the K samples. Also, only one of the Br and three of the Cu values for Q samples are in the range found in the K samples.

The conclusion in this case was that there is no evidence from these data that even one of the hairs found in the car originated from the victim's head. This evidence was introduced at the suspect's murder trial (1968). The hair results were of assistance to the case of the defense, and the defendant was found not guilty. This case represents the first U.S. court case in which NAA results were successfully introduced by the defense.

Table 2. Mean, standard deviation, and range of elemental concentration for eight hair samples from the head of the victim (K samples of Table 1).

Element	Mean (ppm)	Range (ppm)	Range/mean
Copper	13 ± 11	33	2.6
Manganese	22 ± 8	23	1.0
Zinc	860 ± 480	1170	1.4
Sodium	500 ± 360	1040	2.1
Chlorine	910 ± 960	2280	2.5
Bromine	28 ± 12	29	1.0

B. GUNSHOT-RESIDUE DETECTION CASES

This laboratory has extensively investigated the problem of detection of gunshot residues by NAA [6-8]. In addition, many samples from actual criminal cases have been analyzed. Many law enforcement agencies now use a special paraffin gunshot-residue sampling kit, supplied by this laboratory, for testing of the hands of victims and suspects in shooting cases. In gun firings, small amounts of Ba and Sb from the cartridge primer fall on the back of the gun hand. The results from three illustrative cases are collected in Table 3.

The first two cases involve apparent suicides. In the first, a wife (Mrs. S) was found dead, and the husband (Mr. S) was suspected. The levels found on the husband's paraffin handlifts tend to exonerate him, while the Ba and Sb values found on the handlift from the wife's left hand are in the range typical of the firing of a hand gun. Thus, suicide was strongly indicated.

In the second case the Ba and Sb levels found in the victim's handlifts do not indicate that he fired a hand gun. If the hands were undisturbed and the samples correctly taken, it would appear unlikely that the victim fired a hand gun immediately before his death. The five test values shown in Table 3 for this case were values found by test firings of the death gun. In this case, murder was definitely indicated. Unfortunately, no suitable handlift sample from the suspect was available for analysis.

Case 3 of Table 3 involves handlifts from a murder case in which both the Ba and Sb levels found are consistent with the contention that that individual had fired a hand gun. The right hand is clearly higher in these elements than the left. The individual confessed and pleaded guilty.

C. BULLET LEAD COMPARISON CASES

A recent study [9] has employed NAA to measure the Sb content of bullet lead. Trace-element levels of As, Al, and Ag can also sometimes be

Table 3. Barium and Antimony levels found on paraffin lifts obtained during the investigation of three actual crimes.

Case	Description of sample	Hand	Barium found (μg)	Antimony found (μg)
1	Mr. S	Right	0.088 ± 0.003[a]	0.0085 ± 0.0009
	Mr. S	Left	0.138 ± 0.006	0.0127 ± 0.0009
	Mrs. S	Right	0.353 ± 0.007	0.131 ± 0.002
	Mrs. S	Left	0.75 ± 0.01	0.398 ± 0.004
2	Victim	Right	0.096 ± 0.003	0.0122 ± 0.008
	Victim	Left	0.156 ± 0.004	0.0065 ± 0.0009
	Test 1	Right	3.11 ± 0.02	0.395 ± 0.005
	Test 2	Right	0.633 ± 0.009	0.117 ± 0.002
	Test 3	Right	1.71 ± 0.02	0.499 ± 0.006
	Test 4	Right	2.64 ± 0.03	0.542 ± 0.006
	Test 5	Right	1.74 ± 0.02	0.334 ± 0.004
3	Mr. E	Right	0.81 ± 0.01	0.060 ± 0.002
	Mr. E	Left	0.49 ± 0.01	0.025 ± 0.002

[a] The plus–or–minus values shown represent one standard deviation (1σ) of the value, computed only from counting statistics.

detected in samples of bullet lead. Considerable differences in the composition of bullets of different manufacture are found, while bullets from the same box appear quite uniform. Table 4 contains data from three criminal cases in which bullet lead specimens were examined.

In Case 1 of Table 4 the samples were three bullet fragments found at the scene of a crime. It appears from the results of the analyses that the three fragments are either parts of the same bullet or from bullets from the same box.

In the second case, the belief that the bullet removed from the victim came from the same source as the bullets found in the alleged weapon is consistent with the analytical results.

The third case is slightly ambiguous in that although there is good agreement for three elements, the Al level in the bullet removed from the body is outside the range of the Al values in the remaining bullets. This may, however, be the result of sample heterogeneity. The As values from the nine bullets found in the possession of the suspect show an unusually wide spread.

Table 4. NAA of bullet lead specimens involved in three actual cases.

Case	Sample description	Values found Antimony (%)	Silver (ppm)	Arsenic (ppm)	Aluminum (ppm)
1	bullet fragment	0.745	18	N. D.[a]	4
	" "	0.738	16	N. D.	4
	" "	0.739	17	N. D.	6
2	removed from body	0.93	N. D.	125	N. D.
	" " weapon	0.95	N. D.	133	N. D.
	" " "	0.93	N. D.	125	N. D.
	" " "	0.88	N. D.	84	N. D.
	" " "	0.92	N. D.	80	N. D.
3	removed from body	0.96	11	92	12
	Mean and standard deviation of nine bullets in the possession of a suspect	0.97 ± 0.06	13 ± 1	107 ± 116	4.6 ± 1.2

[a] N. D. = Not Detected.

D. A Pigment Analysis of a Painting

The case described involved the analysis of minute flecks of yellow paint taken from an oil painting. The problem involved the discrimination between lead antimonate (Naples Yellow) and a second pigment which is a mixture of lead and tin oxides. The latter type of yellow pigment was used in the time and place in which the questioned painting was alleged to have originated [10].

Two flecks were received for examination. Their weight was estimated from their linear dimensions and approximate density. Table 5 contains these estimated weights and the results of the analyses. No attempt was made to clean the samples. They were manipulated with glass capillary needles on a microscope stage.

The values found for tin and antimony show that the pigment examined contained Sn rather than Sb as a major constituent. The source of the photopeaks detected was verified by comparing both the observed gamma-ray energies and the observed half lives with those of the Sn radionuclides, ^{123m}Sn and ^{125m}Sn (see Table 6).

Table 5. Tin and antimony levels in paint flecks from a painting under investigation.

Sample	Estimated weight (μg)	Values found Tin (μg)	 Antimony (μg)
1	3	0.29 ± 0.01[a]	0.001 ± 0.001[a]
2	10	0.77 ± 0.02	0.005 ± 0.003

[a] Precision of analysis based on counting statistics only.

Table 6. Experimentally-determined half lives of photopeaks from neutron-activated paint flecks.

Sample	Gamma-ray energy (keV)	Experimental half life (min)	Probable Radionuclide Radionuclide	 Literature half life (min)
1	160	38	^{123m}Sn	39.5
1	325	9.5	^{125m}Sn	9.5
2	160	37.5	^{123m}Sn	39.5
2	325	9.5	^{125m}Sn	9.5

E. A CIVIL CASE INVOLVING ALLEGED MERCURY POISONING OF ANIMALS

This 1968 case is of interest not because of the NAA work itself, but rather because it represents the first time in the U.S. that NAA results have been presented in court in a civil suit. Prior to this case, there were some 42 U.S. court cases involving NAA results (the first one taking place in March 1964)—all criminal cases. This $250,000 civil suit was won by the defendant company, and NAA determination of traces of mercury present in oats supplied by the defendant company to the plaintiff was helpful to the defense. The Hg level in the oats was shown to be far too low to have the caused the deaths of the valuable race horses involved in the case.

III. Discussion

The methods employed in analyzing actual case samples by NAA are quite analogous to those employed in many other applications of the method. Small, unique, or contaminated samples may be more common in forensic work, but also are hardly unknown in many other areas in which NAA is applied. The major difficulties encountered in this type of work center about the problems of proper sampling and proper interpretation of the results.

In general, the sample is obtained by a person other than the analyst. In almost every case discussed in this paper, some point regarding the state of the sample when encountered or the precise manner of removal was in need of clarification.

Much of the research and development work in the field of forensic NAA has been involved with investigating large numbers of samples of a particular class of materials, in order to learn in the case of actual case samples the interpretation to be given to the analytical results. For many materials whose sample universe is quite large one can, with suitable data on the samples and a statistically large background of information, calculate the probability that two specimens of evidence material have, or do not have, a "common origin". For many materials NAA has a power to discriminate between samples that are indistinguishable by other analytical methods. In actual cases in which the problem of characterization is the central one, extreme care must be employed by the analyst in conveying both to the submitter of the evidence samples and to the jury, the "probabilistic" nature of his conclusions.

IV. References

[1] Bate, L. C., J. Forensic Sci. **10,** 60 (1965).

[2] Perkons, A. K., in the Proceedings of the First International Conference on Forensic Activation Analysis, edited by V. P. Guinn, 1967, p. 221.

[3] Coleman, R. F., Cripps, F. H., Stinson, A., and Scott, H. D., AWRE Report No. 0-86/66 (IAEA) 1967.

[4] Lima, F. W., Shibata, H., and Atalla, L. T., IAEA Report-72 (IAEA) Geneva, 1964.

[5] Forslev, A. W., J. Forensic Sci. **11,** 217 (1966).

[6] Guinn, V. P., General Atomic Report GA-3491, 1962.

[7] Ruch, R. R., Guinn, V. P., and Pinker, R. H., Nucl. Sci. & Eng. **20,** 381 (1964).

[8] Guinn, V. P., in the Proceedings of the First International Conference on Forensic Activation Analysis, edited by V. P. Guinn, 1967, p. 161.

[9] Lukens, H. R., and Guinn, V. P., submitted for publication in the Journal of Forensic Sciences.

[10] Gettens, R. J., and Stout, G. L., "Painting Materials: A Short Encyclopedia", Dover Publications, New York, 1966, p. 133.

ARSENIC CONTENT OF HUMAN HAIR AFTER WASHING AS DETERMINED BY ACTIVATION ANALYSIS

A. J. van den Berg, J. J. M. de Goeij,
J. P. W. Houtman and Miss C. Zegers

Reactor Instituut
Delft, Netherlands

I. Introduction

In earlier investigation [1] we have measured the mobility of a few trace elements in human hair when this is contacted with aqueous solutions. In the desorption experiments it was found that sodium [2], zinc and chromium contents could be reduced by washing with cold acidified water with a pH between 2 and 6. On the contrary the desorption of arsenic was limited to the amount previously introduced by adsorption. This induced us to start a more thorough research of the desorption of arsenic from hair taking in consideration the various paths through which the arsenic could have been incorporated.

The introduction of arsenic in hair is possible by metabolic processes or by outside contamination. Though these processes are fundamentally different they are, in practice, not always easily distinguishable. Metabolic secretion can also include the contamination of hair from outside by sweat. Contact of a person with arsenic containing dust or moisture may also lead to ingestion and inhalation and then to metabolic secretion into the hair.

For the arsenic content of hair from normal persons strongly varying figures, 0.03 to 2.5 parts per million (ppm), are reported [3-9].

After using arsenic containing drugs or upon deliberate poisoning the arsenic content of newly growing hair is immediately and strongly raised to concentrations up to a few hundred ppm's [9,10].

External contamination with arsenic can take place in industry especially in arsenic ore mines and tin smelting industries. As a result, the hair of the industrial workers can contain up to 1000 ppm without simultaneous concentration increase in the urine [10]. Moreover, external contamination after death has been claimed to occur by arsenic from the soil of the graveyard.

From this it becomes clear that the development of a technique for distinguishing between the various ways of incorporation—for instance by a selected washing procedure— would be very useful.

A few arguments can be given for a difference in behavior during such a washing treatment. Previous experiments [1] have shown that arsenic absorption in the bulk of the hair is only appreciable at $\mathrm{pH} < 3$.[1] Even then it is probably not introduced into the innermost part (medulla). The part of the arsenic incorporated into this medulla by metabolic processes will then also be less easily washed out. Moreover, arsenic introduced by metabolic processes may at least be partly incorporated into the proteins (-S-AsS-; -AsH_2) whereas arsenic introduced from outside may only be bound less strongly in the form of ions to the active groups.

II. Experimental Methods

Wisps of hair (length 1 to 2 cm) were washed with 0.1 *N* HCl at 37 °C. The washing liquid was refreshed regularly. After specific times, 0.03 to 30 mg samples were taken. They were dried between tissue paper and irradiated in the H.O.R. during 1 to 13 hours in a neutron flux of approximately $3 \times 10^{12}\ \mathrm{n \cdot cm^{-2} \cdot sec^{-1}}$. Evaporated samples of an alkaline solution of As_2O_3 were taken as standards. The irradiated samples were weighed and destroyed by $H_2SO_4 + H_2O_2$ after addition of As_2O_3 carrier. The arsenic was separated by distillation as $AsBr_3$. The distillate was purified from antimony by means of Dowex 1X10. In the effluent the As was precipitated by means of $NaPH_2O_2.H_2O$. After filtration the precipitate was dissolved in H_2O_2 and counted during 5 to 120 min in a 3 in. × 3 in. NaI(Tl) well counter in combination with a 400 channel analyzer. The chemical yield was determined by titration with lead nitrate using P.A.R. as an indicator.

The experiments were carried out with hair from various sources as is shown in Table 1.

III. Results and Discussion

A. EXPERIMENTS WITH HAIR OF NORMAL PEOPLE

These were carried out using hair types A, B and H. Results of washing experiments are shown in Figures 1, 2 and 3. Hair types A and H (Fig. 1 and 2) did not show a significant decrease in arsenic content whereas hair B (Fig. 3) showed a loss of approximately 10%. Hair types A and B[2] were

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[1] Compare also Table 2. The increased uptake of As between pH 6 and 10 from a solution of As^V in deionized instead of distilled water as published in an earlier article [1] has afterwards been found to be an increased uptake of Cu present in the deionized water.

[2] The washing treatment with hair B has been repeated recently. It lead to a loss in As of approximately 40%. This hair was probably contaminated with As as is indicated in Table 1. It is confirmed by the high As content as compared to the hair of eleven workers in our laboratory which contained between 0.5 and 0.15 ppm.

Table 1. Hair types used.

Sample	Origin	Sex	Date of birth	As content (ppm)	History
A	Dutch	female	1946	0.10	No contact with As
B	"	"	1935	1.8	Person involved in As Research
E[a]	British	male	–	10–80	Patient, received 56 mg As_2O_3 over 80 days
F[b]	Brazilian	"	1925	400	Worker (No. 8) in As industry during 17 years
G[b]	"	"	1928	56	Worker (No. 15) in As industry during 7 years
H	Dutch	female	1919	0.09	No contact with As

[a] Kindly put at our disposal by Dr. J. O'D. Alexander and Dr. J. M. A. Lenihan, Glasgow

[b] Kindly provided by Dr. F. W. Lima, Sao Paulo

impregnated with As^V solution of various strengths and at various pH. The impregnated hair was subsequently washed. Results are shown in Table 2. They indicate that at least 93% of the impregnated arsenic is again removed in the washing treatment. In most experiments the arsenic content after 400 and 1600 minutes of desorption was still found somewhat higher than the original concentration. However, the ultimate values obtained were all below a few ppm's. A typical desorption curve is shown in Figure 4. In the experiments with hair B in which shorter impregnation times were applied, the curve showed a very steep gradient at the start indicating that the arsenic was deposited with some preference in the outer region of the hair.

B. Experiments with Hair of People Who Had Received an Oral Dose of Arsenic

These experiments were carried out with a few single hairs of type E. First the distribution of arsenic over one of these hairs was determined. The results are given in Figure 5. On the basis of these results the pieces between 0.5 and 3 cm and those between 3 and 8 cm from the root were collected from four other hairs. These pieces were further cut to lengths of 1 cm and homogenized. Both fractions were then washed during 1600 minutes in duplicate experiments. The results are given in Table 3. They

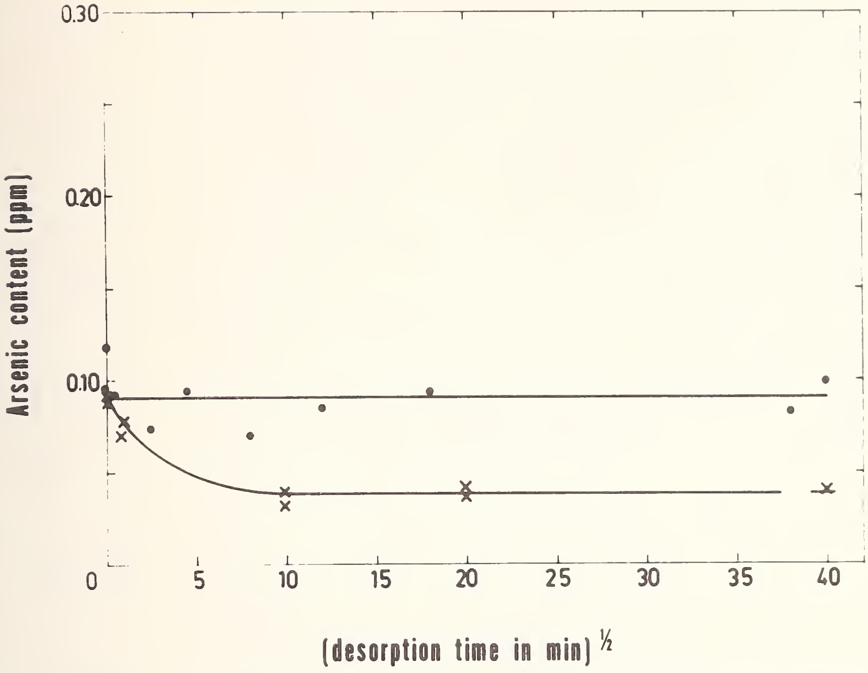

Figure 1. Desorption curves for hair type A; • = 0.1 *N* HCl at 37 °C; X = water at 76 °C.

show that here only between 10 and 40% of the total amount of arsenic could be desorbed. As a result very considerable amounts of arsenic are left especially when high amounts were originally present.

C. EXPERIMENTS WITH HAIR OF PEOPLE WORKING IN THE ARSENIC INDUSTRY

These were carried out with hair types F and G. The results are given in Figures 6 and 7. They show that also here the arsenic is only desorbed for approximately 50%. As it may be assumed that this arsenic is also incorporated for the most part by outside contamination, [10] these results are in strong contradiction to those described in paragraph A. It would mean that either the time of presence of arsenic in hair influences the bond strength or that arsenic containing dust behaves differently from an aqueous solution. In this respect it is worth mentioning that it is possible to contaminate hair to a content of 5.5 and 0.75% respectively simply by shaking during 75 hours with solid As_2O_3 and As_2O_5 powder, followed by brushing and wiping (Kleenex). It could be proven by x-ray diffraction that parts of these contaminations were still present in the form

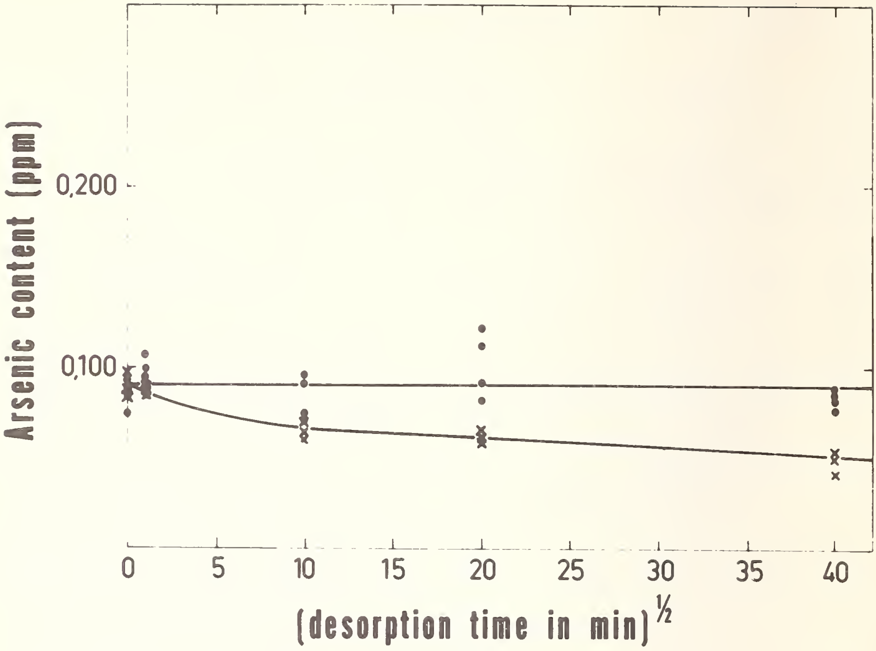

Figure 2. Desorption curves for type H; • = 0.1 *N* HCl at 37 °C; X=water at 76 °C.

of the original oxides. Moreover, the contaminations could be removed by 0.1 *N* HCl (37 °C) and water (76 °C) for more than 99 percent. Therefore, the dust involved in the hair types F and G is either of a less soluble type or has reacted with the hair proteins during the prolonged time of contact. Contamination of the hair from outside by insoluble powderous substances will probably lead to an increased surface concentration. Therefore, the measurement of the radial distribution of the arsenic in hair may provide an additional possibility of distinguishing between hair in which the arsenic is deposited metabolically or through external contamination by an insoluble As-containing dust.

An attempt by measuring the radial distribution of the arsenic after shaking with As_2O_3 and As_2O_5 was made by abrasion experiments [1]. Some preliminary results are given in Figure 8. They indicate that As_2O_3 is deposited more at the outside than As_2O_5, probably because the latter is more hygroscopic. The hair of one industrial worker seems also to show a higher outside concentration.

However, more work in this field has to be done before definite conclusions from such measurements can be made.

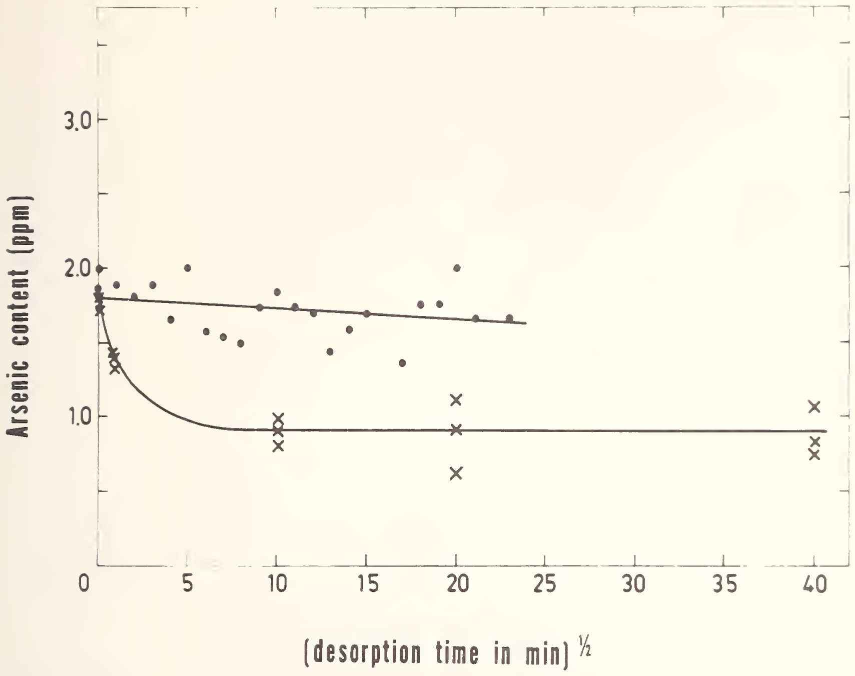

Figure 3. Desorption curves for hair type B; • = 0.1 *N* HCl at 37 °C; X = water at 76 °C.

Table 2. Absorption–desorption experiments with normal hair.

Hair type	Original As content (ppm)	Absorption			Arsenic content of the hair in ppm after different washing times (min)				
		pH	concentration	time (h)	0	1	100	400	1600
A	0.1	2.0	3 ppm	67	29	26	5.7	2.2	2.0
A	0.1	2.0	300 ppm	67	5270	5100	349	12.4	7.8
A	0.1	4.35	3 ppm	67	5.3	3.8	1.7	1.2	0.93
A	0.1	4.35	300 ppm	67	250	203	23	12	4.6
A	0.1	7.2	2 ppm	67	0.69	0.64	0.14	0.07	0.07
A	0.1	7.2	200 ppm	67	47	32	1.3	0.40	0.30
A	0.1	9.6	2 ppm	67	0.58	0.50	0.15	0.09	0.08
A	0.1	9.0	200 ppm	67	59	36	3.9	2.0	1.9
B	1.8	4.35	3 ppm	40	101	6.5	2.3	1.4	–
B	1.8	4.35	30 ppm	40	156	34	9	3.2	–
B	1.8	4.35	300 ppm	40	245	215	15	7.2	–

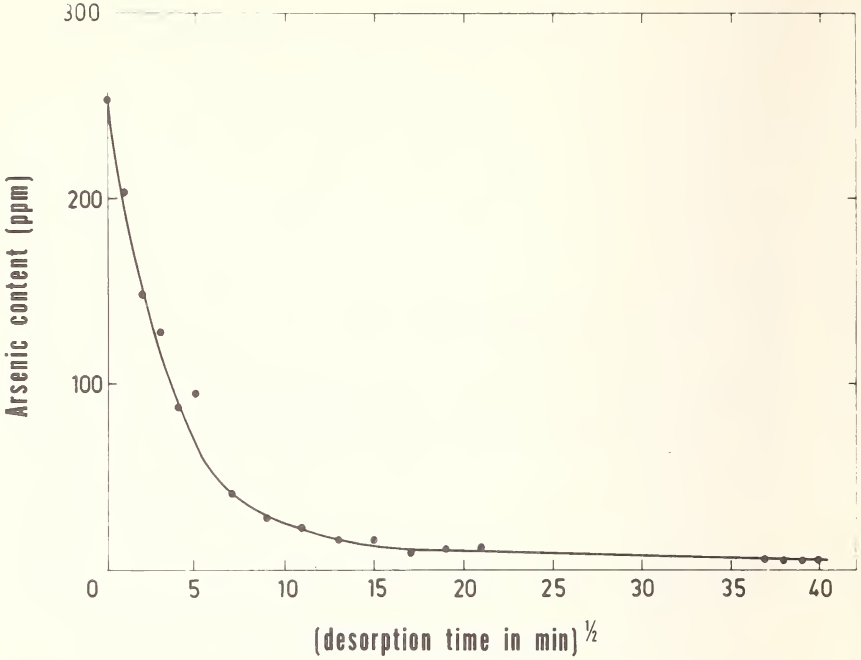

Figure 4. Desorption curve for hair type A after impregnation with a 300 ppm As^{V} solution at pH 4.35.

IV. Comparison with Results of Other Investigations

Comparable work has been carried out by Dr. Lima [10] who applied a washing procedure with pure water at 76 °C. He compared the behavior of rabbits hair containing metabolically secreted arsenic, hair from workers in the arsenic industry and hair which was contaminated from outside by either As_2O_3 powder or an arsenate solution. Though he found increasing percentages of desorbed arsenic in this sequence (64, 83 and 95%) he concluded that his washing treatment could not distinguish between metabolically secreted and impregnated arsenic. For reasons of comparison we have also applied Lima's desorption technique to some of our samples (compare Figs. 1, 2, 5, 6.) The results indicate that a treatment with pure water at 76 °C is a rather severe one which could obscure relatively small differences in behavior of arsenic introduced by different ways. In this respect it is important that the chemical and structural composition of the hair is not damaged by the desorption treatment. From this point of view the technique using 0.1 *N* HCl at 37 °C is certainly preferable—perhaps it is not an optimal procedure. More

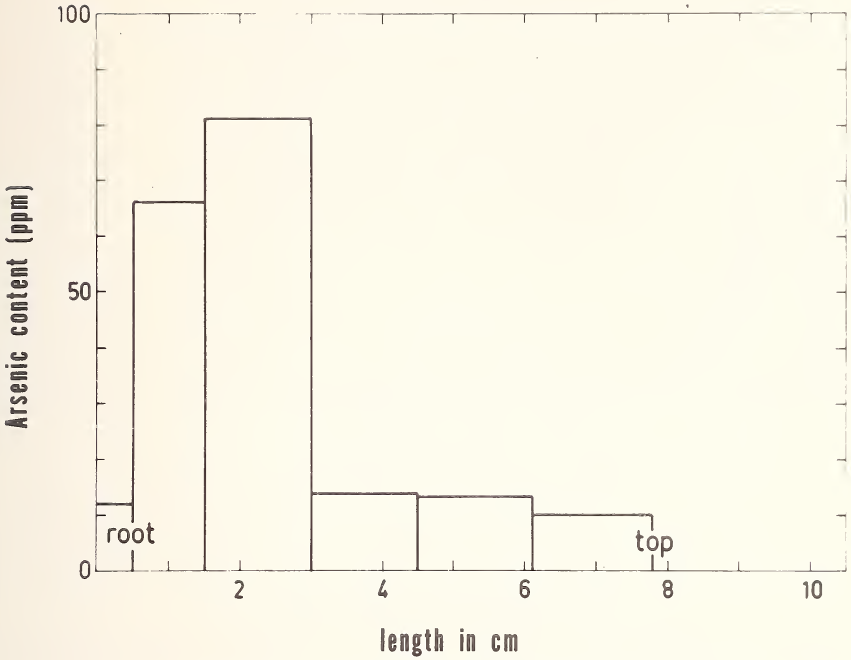

Figure 5. Sectional analysis of a single hair type E.

Table 3. Description experiments with hair of a person who has received an oral dose of arsenic.

Part of the hair	Sample weight	Arsenic content of the hair in ppm before and after washing	
		before	after 1600 min
0.5–3.0 cm	0.15 mg	80.4	72.3
0.5–3.0 cm	0.15 mg	86.8	50.7
mean value		83.6	62.8
3.0–8.0 cm	0.30 mg	15.4	10.6
3:0–8:0 cm	0:30 mg	14.5	11.4
mean value		15.0	11.0

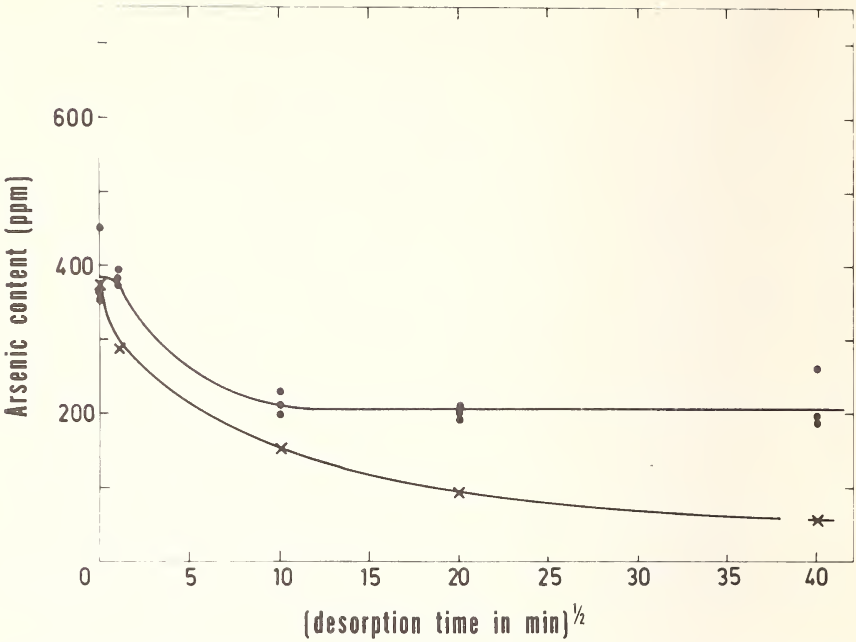

Figure 6. Desorption curves for hair type F; • = 0.1 *N* HCl at 37 °C; X = water at 76 °C.

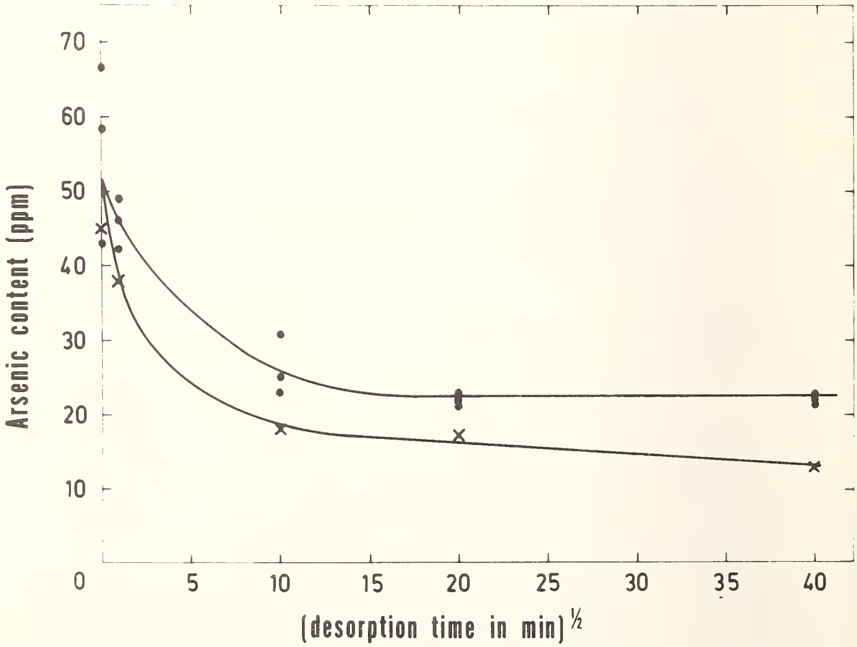

Figure 7. Desorption curves for hair type G; • = 0.1 *N* HCl at 37 °C; X = water at 76 °C.

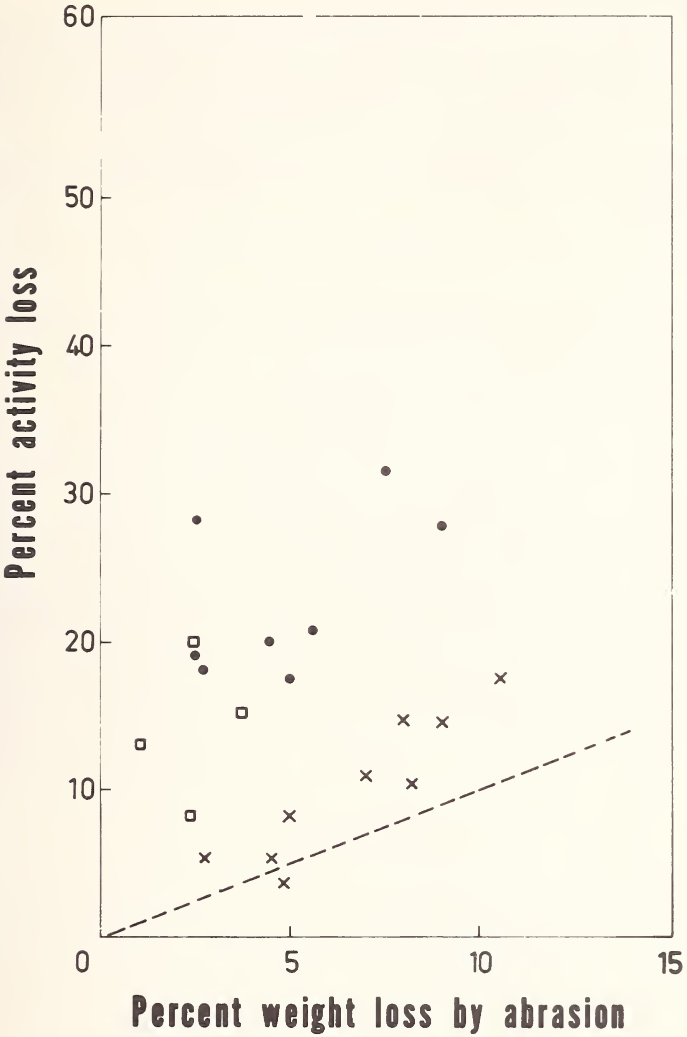

Figure 8. Arsenic distribution in outermost layers of hairs.

---- Theoretical for homogeneous distribution.

X Hair type B contamination with As_2O_5.

• Hair type B contaminates with As_2O_3.

□ Hair type G.

extensive research with various hair samples and washing liquids seems necessary.

V. Acknowledgment

Thanks are due to J. J. Kroon and M. G. Serrus for their assistance in this research.

VI. References

[1] Berg, A. J. van den, Bruin, M. de, and Houtman, J. P. W., Proc. of the Symposium on Nuclear Techniques in the Life Sciences, Amsterdam (May 1967), I.A.E.A. Vienna (1967), p. 661.
[2] Houtman, J. P. W., Science **156,** 1397 (1967).
[3] Young, E. G., and Rice, A. H., J. Lab. Clin. Med. **29,** 429 (1944).
[4] Mackintosh, W. C., and Jervis, R. E., A.E.C.L.-1083 (1960).
[5] Smales, A. A., and Pate, B. D., Analyst **77,** 196 (1952).
[6] Szep, O., Z. Physiol. Chem. **267,** 401 (1940).
[7] Lenihan, J. M. A., Proc. of the Symposium on Radiactivation Analysis, Vienna (June 1959), Butterworths, London (1960), p. 81.
[8] Lenihan, J. M. A., and Smith, H. A., Proc. 2nd Int. Conf. on Peaceful Uses of Atomic Energy, Geneva 1958, United Nations, New York **26,** 238 (1959).
[9] Shapiro, H. A., J. Forensic Medicine **14,** 65 (1967).
[10] Atalla, L. T., Silva, C. M., and Lima, F. W., Anais da Academia Brasileira da Ciencias **37,** 433 (1965).

COMPARISON OF ACTIVATION ANALYSIS AND SPARK SOURCE MASS SPECTROMETRY FOR FORENSIC APPLICATIONS

T. G. Williamson and W. W. Harrison

University of Virginia
Charlottesville, Virginia 22901

I. Introduction

Neutron activation analysis and spark source mass spectrometry are being compared on samples of interest to the forensic scientist. The purpose is to investigate the two techniques with respect to characterization of samples, precision and reproducibility of data, amount of sample required, sample handling and time for analysis. Specifically, the two methods of analysis have been compared on human hair samples and will be used on fibers, glass, paint chips, *etc*. A considerable amount of past work has been done on hair by activation analysis; however, essentially no work has been done by spark source mass spectrometry and it was felt that this would be a good place to start.

Irradiations were done in the one megawatt swimming pool reactor at the University of Virginia. The mass spectrometer is a AEI MS-702 spark source mass spectrometer at the University.

II. Experimental

The samples are all prepared in the Chemistry Laboratory in a clean environment to eliminate analysis errors arising from differences in sample treatment which might occur if separate samples were prepared in two laboratories. Hair samples are cleaned by washing for one hour in a one per cent non-ionic detergent solution, rinsing with one liter de-ionized water and dried at 100 °C. Several strands of hair are placed in polyethylene vials that have been cleaned in a detergent solution, de-ionized water and acetone and sent to the reactor for irradiation. The samples are irradiated in a thermal neutron flux of 1.7×10^{13} $n \cdot cm^{-2} \cdot sec^{-1}$ for periods of 10 minutes and 1-4 hours. The samples are removed from their polyethylene vials and are counted throughout their decay with wait times as short as 3 minutes. The activities are determined by peak area integration and least squares fitting to the decay curves. The 10 minute irradiation is used to detect aluminum, bromine, chlorine, magnesium (by stripping the 0.84 MeV decay curve) and the presence of sulfur and calcium. The 5.07 minute ^{37}S activity decays by emission of a 3.09 MeV gamma ray in 90% of its disintegrations and the 8.8 minute ^{49}Ca isotope emits a 3.10 MeV gamma ray in 89% of its disintegrations and a 4.1 MeV gamma ray in 10% [1]. The 4.12 MeV ^{24}Na sum peak interferes with the latter gamma ray making it difficult to separate the sulfur from the calcium activity in a short irradiation. It should be noted that calcium concentrations of about 2,000 parts per million (ppm) have been reported [2] and since sulfur is a major constituent its concentration is about 10 times as great as that of calcium [3]. The cross sections and abundances of the activating isotopes are such that the activities of the two elements would be about the same.

The four hour irradiation is counted over several days and used to calculate concentrations of copper, gold, manganese, sodium, and zinc.

For analysis by the mass spectrometer hair samples of about one-half of a gram have been used. These are minced by chopping with a stainless steel scalpel and mixed to provide a homogeneous representative sample. The hair is then ashed in a muffle furnace at 450 °C overnight to eliminate background hydrocarbon spectra. The ash is then mixed with a suitable matrix for shaping into an electrode for analysis. Both high purity silver (99.999+%) and USP grade graphite (Ultracarbon Corp.) have been used. The powdered silver is much easier to handle, forms much more stable electrodes and sparks more profusely. However, the trace element contamination is significantly higher than for graphite and the silver also suffers from a larger powder particle size than graphite which made the preparation of homogeneous electrodes difficult.

In the present procedure a one to one mixture of USP graphite-hair ash is mixed with a Teflon spatula and transferred to a vial on a mechanical mixer where it is homogenized for 20 minutes. A portion of the mixture is "tipped out" in a stainless steel die using a polyethylene plug to eliminate contamination. Graphite is placed on top of the tip mixture and electrodes formed at 10-20 tons pressure.

The electrode is sparked in the mass spectrometer for a series of graded exposures. To obtain quantitative results the ion beam chopper, which allows careful control of the ion beam by pulsing the ion flux on the readout plate rather than allowing a single intense charge to accumulate is used. The photographic plate is then read by a densitometer and the data analyzed with a Burroughs B5500 computer. A similar background run is made using an electrode prepared in the same manner without the addition of the hair ash. Calibration is performed by analyzing a sample of the minced, homogenized hair by atomic absorption for one element, usually copper. The analysis program then (1) calculates and plots a calibration curve for the photo plate to correct for variation in response with exposure, (2) corrects data to this calibration, (3) corrects for background exposure, (4) corrects for isotopic abundance of each element, (5) correlates exposure differences, (6) corrects for atomic weight ratio between element and standard, (7) corrects for the mass response of the photo plate, (8) corrects for the area of the selected line, (9) compares these corrections to a standard calibration element and computes concentrations and (10) prints the results in parts per million by weight.

III. Results and Discussion

A typical plate taken with the mass source spectrometer is shown in Figure 1 on which the elements identified in this specimen are marked.

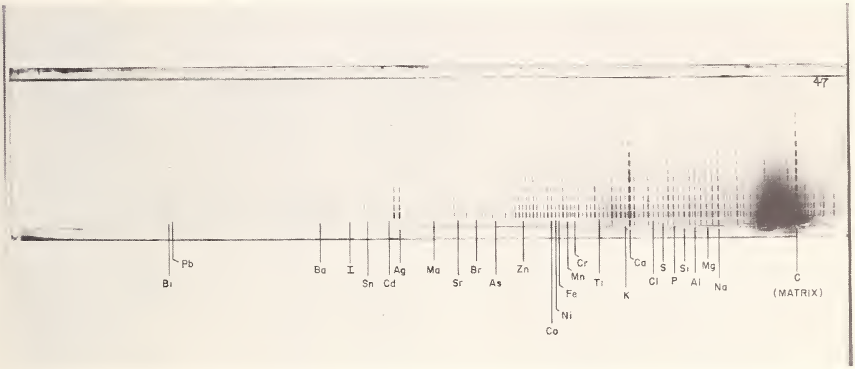

Figure 1. Typical SSMS plate-hair sample.

The other lines correspond to multiple ionization states or polyatomic combinations of the elements known to be present and supply no additional information. Several different hair samples have been run by spark source mass spectrometry and compared to activation analysis runs. Some typical results on hairs from the same person and prepared in the same manner are shown in Table 1, which lists the concentrations by weight of 22 elements detected by mass spectrometry and 8 elements by neutron activation analysis. The agreement is reasonable with the exception of manganese and there is the possibility of a hydrocarbon interference in the mass spectrometer data. This interference may also affect the titanium and barium results.

The advantages of neutron activation analysis to the forensic scientist in characterizing evidence material have often been listed. Coleman, *et al* [2] list 12 elements they have used to characterize hair and Perkons [4] lists 20 elements that he finds using a NaI scintillation crystal, and 23 elements [5] using a Ge(Li) detector. These were obtained from long irradiations in a high flux reactor and long decay times. We list 8 elements that can be detected from single strands of hair with delays between the irradiation and final analysis of about one week. The mass spectrometer gives quantitative information for at least 22 elements in hair, with an analysis time of less than two days, *i.e.*, if a hair sample is received one day, it can be ashed overnight and the complete analysis done the following day. On the other hand the spark source mass spectrometer does not preserve the hair, it is destroyed when sparked, and it requires a larger quantity than the activation analysis. We are presently investigating techniques for reducing the amount of sample required for analysis.

This work is continuing, to investigate the precision of the data obtained, to determine what elements are most useful for identification by

Table 1. Comparison of hair analyzed by SSMS and NAA.

	Concentration, ppm	
Element	SSMS	NAA
Aluminum	41	25
Magnesium	262	180
Silicon	146	–
Chlorine	–	230
Phosphorous	141	–
Sodium	199	170
Calcium	1754	–
Manganese	16	1.5
Bromine	1.3	4.5
Chromium	7.7	–
Titanium	87	–
Nickel	2.6	–
Cobalt	4.5	–
Zinc	367	81
Arsenic	2.2	–
Strontium	37	–
Molybdenum	0.82	–
Tin	71	–
Iodine	0.95	–
Barium	111	–
Tungsten	4.4	–
Lead	67	–
Gold	–	0.40
Copper	22.6	9.6

the spark source mass spectrometer, and to further investigate the relative advantages of the two techniques with respect to their abilities to distinguish one evidence sample from another.

IV. Acknowledgment

This work is sponsored by the Office of Law Enforcement Assistance under Grant No. 154.

V. References

[1] Lederer, C. M., Hollander, J. M., and Perlman, I., Table of Isotopes, Sixth Edition, John Wiley and Sons, Inc., New York, 1968.
[2] Coleman, R. F., *et al*, AWRE 0-86/66, 1967.
[3] Spector, W. S., Handbook of Biological Data, Saunders, Philadelphia, 1956.
[4] Perkons, A. K., Proceedings of the First International Conference on Forensic Activation Analysis, GA-8171, 1967, p. 221.
[5] Perkons, A. K., and Jervis, R. E., Trans. Am. Nucl. Soc. **11**, 82 (1968).

CHAPTER 4

GEOCHEMICAL AND COSMOCHEMICAL APPLICATIONS

Synopsis of Discussions

HIROSHI HAMAGUCHI, *Chairman*

Department of Chemistry
University of Tokyo
Tokyo, Japan

Geochemical and cosmochemical applications of activation analysis covered many different determinations of many elements in different kinds of materials, and the proper grouping is quite difficult.

Most of the papers were concerned with multielement determinations, and efforts have been undertaken by a number of research groups to extend the number of elements which can simultaneously be measured. Work along this line has been done by groups from Purdue University, University of Oregon, MIT and their collaborators, and the University of Vienna.

The high resolution Ge(Li) detectors have been extensively used in most of these investigations. Thus, the University of Oregon group, using a large coaxial Ge(Li) detector of 30 cm^3 volume, could determine 23 elements by a purely instrumental technique. Also the MIT group extended the use of Ge(Li) detectors in instrumental neutron activation analysis to very short-lived species. However, the photopeak efficiency of Ge(Li) detectors is usually much lower than that of the conventional NaI(Tl) scintillators. A question is raised here as to just how far the technique of nondestructive analysis could be extended. It was suggested by Dr. G. E. Gordon that unless a very high resolution detector is used, the concentrations of many additional elements could not be determined in geological samples. The use of Ge(Li) detectors coupled with an anti-Compton shield, and also Ge(Li)-NaI(Tl) coincidence counting have been suggested for the next major advances in the technique for improving selectivity.

Another way to improve the sensitivity is to incorporate simple group chemical separations in order to diminish the background and eliminate spectral interferences. Use of chemical separation procedures seem to be increasing. For example, our group showed that a simple chemical group separation had made possible the simultaneous determination of the chemically coherent elements with increased sensitivity. The Washington

State University group measured eighteen elements in rocks after partial chemical processing to remove interfering ^{24}Na, and the Purdue University group reported a separation scheme to measure seventeen elements in standard rocks after separating into several groups by combining distillation, solvent extraction, and ion exchange techniques. Also Dr. W. Kiesl of the University of Vienna has reported an analytical scheme for complete mutual separation of eighteen elements in meteorites.

The nondestructive determination by the γ-γ coincidence technique has been used for specific elements in the following two presentations: The University of Kentucky group has reported the determination of iridium in meteorites for the purpose of checking the various literature values which show large variation. The group of the Institute for Atomic Energy, Norway has presented the determination of some rare earths in rocks and minerals, and it was shown that the method is now routinely used for europium determinations.

The group of U. S. Geological Survey, Denver spoke on the determination of protactinium-231 by neutron activation and alpha spectrometry. The method results in being able to date Pleistocene deposits.

Dr. R. E. Wainerdi of Texas A&M University has presented two papers: one on the geochemical survey of rock samples and the other is on the volcanological studies. It is shown that the geological mapping is made possible by investigating trace element profiles, just as in the case of hair characterization in forensic science.

Dr. H. T. Millard of the U. S. Geological Survey, Denver reported on the nondestructive neutron activation analysis of individual cosmic spherules, and showed that the concentration ratios (trace elements : iron, the major component) could be a measure which differentiates this kind of tiny extraterrestrial materials from terrestrial contaminants.

Other papers presented were routine analysis of some of the major and also minor constituents by Dr. H. A. Das and the nondestructive analysis of aluminum and silicon in meteorites by Dr. S. Meloni.

A specific technique for *in situ* elemental analysis has been presented by Dr. J. W. Mandler of IIT Research Institute, Chicago. This is a combined neutron experiment simultaneously employing capture gamma-ray analysis, activation analysis, inelastic neutron scattering, and thermal neutron die-away techniques for remote analysis. These techniques which are being developed for lunar and planetary surface analysis have been tested for terrestrial applications in geology.

Faced with the many different determinations of trace elements in different kinds of materials, a really pertinent problem with the techniques used here is that of relative measurement in terms of precision and absolute measurement in terms of accuracy. Considerable discussions ensued on this question. Referring to the rare earths, it is pointed out that the measurements should be, relative to each other, as good as possible (*e.g.* at the ± 1% level), in order to be meaningful in interpreting processes in rocks and minerals. Someone quoted an accuracy of ± 1%, but others do not believe that this level of accuracy can be reached in this type of multielement analysis. It is also pointed out that activation analysis is highly useful but does not cover every case. Perhaps, then, we should use a combination of analytical techniques.

ROUTINE DETERMINATIONS OF Al, K, Cr, AND Sn IN GEOCHEMISTRY BY NEUTRON ACTIVATION ANALYSIS

H. A. Das, J. G. van Raaphorst and H. J. L. M. Umans

Reactor Centrum Nederland
Petten (N.H.) Nederland

I. Introduction

A. DETERMINATION OF MAJOR CONSTITUENTS

The routine determinations performed in our laboratory as a service to geologists are listed in Table 1. All analyses start with samples of 100-200 mg, except that of potassium. Two of these procedures are discussed here in more detail; those for aluminum and potassium. In the former analysis there is the problem of correcting for the variation of the total dead time during measurement. The determination of potassium is carried out by

Table 1. Summary of the principal routine analyses on silicate samples.

Element	Radionuclide used	Flux	Irradiation time	Maximal no. of samples irradiated simultaneously	Cooling time	Decomposition of the sample	Chemical separation	Detector
Sodium	^{24}Na	2×10^{10}	1 h	50	24 h			NaI
Magnesium[a]	^{27}Mg	2×10^{13}	5 min	1			Precipitation of Mn with carbamate. Extraction with oxine.	"
Sodium[b]	^{24}Na	10^9	30 min	6	2 h			"
Aluminum	^{28}Al	2×10^{10}	10 sec	1	5 sec			
Silicon[b]	^{28}Al	10^9	30 sec	1 – 6	30 sec			
Phosphorus	^{31}P	10^{10}	17 d	100	2 wks	Na_2CO_3 K_2CO_3	Precipitation as $MgNH_4(PO_4)$	G.M.
Potassium	^{42}K	2×10^{13}	10 min	10	30 h			β–scintillator
						HF	Cation exchange	NaI
Calcium	$^{47}Ca \rightarrow {}^{47}Sc$	"	2–7 d	100	2 wks	Na_2CO_3 K_2CO_3	Extraction with HDEHP	"
Scandium	^{46}Sc	"	" "	100	" "	"		Si(Ge)
Titanium[c]	^{51}Ti	"	5 min	1				NaI
Chromium	^{51}Cr	"	2–7 d	100	2 wks	Na_2O_2	Extraction of perchromate with ethylacetate	"
Manganese	^{56}Mn	2×10^{10}	1 h	50	1 h			NaI
Iron	^{59}Fe	2×10^{13}	2–7 d	100	2 wks			Si(Ge)
Cobalt	^{60}Co	"	" "	100	2 wks			"
Copper	^{64}Cu	10^{11}	4 h	50	2 h	Na_2CO_3 K_2CO_3	Extraction of Cu I with neocuproine	NaI
Zinc	^{65}Zn	2×10^{13}	2–7 d	100	2 wks	"	Anion exchange	"

Table 1. Summary of the principal routine analyses on silicate samples. (continued)

Element	Radionuclide used	Flux	Irradiation time	Maximal no. of samples irradiated simultaneously	Cooling time	Decomposition of the sample	Chemical separation	Detector
Germanium	^{77}Ge	"	20 min	10	30 min	Na_2O_2	Extraction of $GeCl_4$ with CCl_4	"
Bromine	^{80}Br	"	10 min	1		Na_2O_2	Extraction of Br_2 with CCl_4	"
Rubidium	^{86}Rb	2×10^{13}	2–7 d	100	2 wks	Na_2CO_3 K_2CO_3	Precipitation of interfering elements	"
Strontium[a]	^{87m}Sr	10^{11}	2 h	10	1 h		Precipitation of $SrSO_4$ and double act. anal.	"
Tin	$^{113m}Sn \rightarrow {}^{113m}In$	2×10^{13}	2–7 d	100	2 wks	Na_2O_2	Anion exchange	"
Antimony	^{124}Sb	"	" "	100	" "	Na_2CO_3 K_2CO_3	" "	"
Iodine	^{128}I	"	10 min	1		"	Extraction of I_2 with CCl_4	
Cesium	^{134}Cs	"	2–7 d	100	" "	"	Precipitation of interfering elements	"
Barium[a]	^{139}Ba	10^{11}	2 h	10	1 h	"	Precipitation of $BaSO_4$ and double act. anal.	"
Cerium	^{141}Ce	2×10^{13}	2–7 d	100	2 wks	"	Extraction with HDEHP + EDTA	"
Gold	^{198}Au	"	" "	100	2 wks		Red. to element	"
Thorium	$^{233}Th \rightarrow {}^{233}Pa$	"	" "	100	2 wks			"

[a] Chemical pretreatment, dissolved in HF and HNO_3.

[b] All irradiations performed in the reactor except those indicated by "b" which were irradiated in the neutron generator.

[c] Chemical pretreatment, dissolved in HF and adsorbed on DOWEX–2.

Remarks:
1. Samples irradiated at low integrated fluxes (3×10^{17} n/cm^2) are packed in polyethylene, otherwise quartz is used.
2. Standards for short irradiations are weighed–out amounts of pla. compounds. For long irradiations use is made of 100 λ portions of standard solutions, dried on p.a. Al–foil.

beta measurements on small samples (20-30 mg) with standardized counting equipment.

B. DETERMINATION OF TRACE ELEMENTS

When dealing with large series of samples a certain choice of trace elements must be made. Table 1 gives the elements covered by our routine program. In this text two of the determinations involved are discussed; those of chromium and tin. In both analyses a rigorous chemical isolation has to be carried out to eliminate the interfering activities.

II. Dead Time Corrections and the Accuracy of Aluminum and Silicon Determinations

A. GENERAL

The automatic dead time correction of multichannel analyzers is based on the lengthening of the counting time. It does not entirely compensate the effect of dead time in the case of appreciable decay during measurement. The residual effect can be calculated if the observed total dead time is completely due to the radionuclide which is to be measured (see Table 2).

Table 2. Composition of the gamma ray activity of an average silicate sample.

Element	Average abundance (%)	Radionuclide	$T_{1/2}$	Induced activity	Contribution in % to the total activity		
					t_2=0	t_2=30m	t_2=30h
Aluminum	8.1	^{28}Al	2.3 min	195 mC	99.2	2	–
Iron	5.0	^{59}Fe	45.1 d	10^{-4}	–	–	–
Calcium	3.6	^{48}Ca	8.8 min	5.10^{-4}	–	0.5	–
Sodium	2.8	^{24}Na	15 h	0.3	0.2	60	98
Potassium	2.6	^{42}K	12.5 h	0.15	0.1	3	2
Magnesium	2.1	^{27}Mg	9.5 min	0.4	0.2	4	–
Titanium	0.4	^{51}Ti	5.8 min	0.15	0.1	0.5	–
Manganese	0.1	^{56}Mn	2.6 h	0.35	0.2	30	–

Note: Calculations are based on the irradiation of one gram sample during ten minutes at a thermal neutron flux of 2.10^{13} n $\cdot$ cm^{-2} $\cdot$ sec^{-1}.

B. FORMULATION

The influence on measurements without automatic correction is given by the factor f_τ

$$f_\tau=\frac{1-D_0}{D_0(1-e^{-\lambda T_m})}\ln\left[\frac{1}{(1-D_0)+D_0e^{-\lambda T_m}}\right] \tag{1}$$

D_o stands for the total dead time fraction at the beginning of the measurement. It can be read from the analyzer. T_m is the preset counting time. With automatic correction the effect of dead time is equal to f'_τ

$$f'_\tau=\frac{1-D_0}{D_0(1-e^{-\lambda T_m})}\ln\left[\frac{1}{(1-D_0)+D_0e^{-\lambda T'_m}}\right] \tag{2}$$

T'_m is the extended counting time, related to T_m and D_o by equation (3).

$$T_m/T'_m=1+\frac{1}{\lambda T'_m}\ln\left[(1-D_0)+D_0e^{-\lambda T'_m}\right] \tag{3a}$$

$$D_0=\frac{1-e^{-\lambda(T'_m-T_m)}}{1-e^{-\lambda T'_m}} \tag{3b}$$

The derivation of these formulae are available upon request [1-3]. Table 3 gives f_τ and f_τ' as a function of λT_m for various values of D_o. Table 4 applies to the ratio T_m'/T_m'. The D_o values of samples and standards should be roughly equal, and corrections for differences should be applied. A statistical error ($\pm\overline{\Delta D_0}$) leads to an uncertainty in the analyses equal to

$$\epsilon=\frac{\Delta\bar{D}_0(\partial\bar{f}_\tau/\partial\bar{D}_0)\lambda T_m}{\bar{f}_\tau} \tag{4}$$

or

$$\epsilon=\frac{\Delta\bar{D}_0(\partial\bar{f}_\tau'/\partial D_0)\lambda T_m}{\bar{f}_\tau'} \tag{5}$$

$\bar{D}_0$, $\bar{f}_\tau$, and $\bar{f}_\tau'$ denote the average values within a series of measurements.

Table 3. The factors f_τ and f_τ' as a function of λT_m for different values of D_o.

f_τ — λT_m ⟶

D_o	0	0.5	1	2	∞
0.05	0.950	0.956	0.968	0.973	0.977
0.10	0.900	0.921	0.932	0.941	0.949
0.20	0.800	0.834	0.856	0.878	0.893
0.30	0.700	0.744	0.775	0.812	0.831
0.40	0.600	0.653	0.691	0.737	0.765
0.50	0.500	0.557	0.603	0.655	0.683
0.60	0.400	0.456	0.503	0.563	0.611

f_τ'

D_o	0	0.2	0.5	1	∞
0.05	1.000	0.998	0.991	0.983	0.977
0.10	1.000	0.990	0.981	0.969	0.949
0.20	1.000	0.977	0.950	0.928	0.893
0.30	1.000	0.963	0.923	0.885	0.831
0.40	1.000	0.947	0.890	0.833	0.765
0.50	1.000	0.917	0.846	0.779	0.683

C. CALCULATION

Clock and dead time meter of the analyzer are calibrated using Equation (3b) and Table 4. Results for an Intertechnique SA 400 are:

a) Absolute error in T_m is $\Delta T_m = 0.5$ sec.

b) $D_{read}/D_{calculated} = 1.013$, standard deviation 0.04. When comparing

Table 4. The ratio T'_m/T_m as a function of λT_m for various values of D_o.

	λT_m ⟶				
D_o	0	0.2	0.5	1	2
0.05	1.053	1.048	1.042	1.038	1.025
0.10	1.111	1.100	1.090	1.075	1.025
0.20	1.250	1.225	1.190	1.145	1.095
0.30	1.429	1.375	1.310	1.238	1.155
0.40	1.667	1.575	1.470	1.352	1.225
0.50	2.000	1.832	1.665	1.485	1.308

the activity of standards and samples, $\overline{\Delta T_m}$ is 0.6 sec and $\overline{\Delta D_0}$ equal to 0.05. In Figure 1 the total error due to $\overline{\Delta T_m}$ and $\overline{\Delta D_0}$ in the automatically corrected measurement of ^{28}Al is given as a function of counting time for various values of D_0. The best value of the counting time is 40-60 sec.

D. EXPERIMENTAL AND RESULTS

A fast rabbit system with 8 mm × 11 mm polyethylene containers is used. Thermal neutron flux is 2×10^{10} n·cm^{-2}·sec^{-1}, irradiation time 10

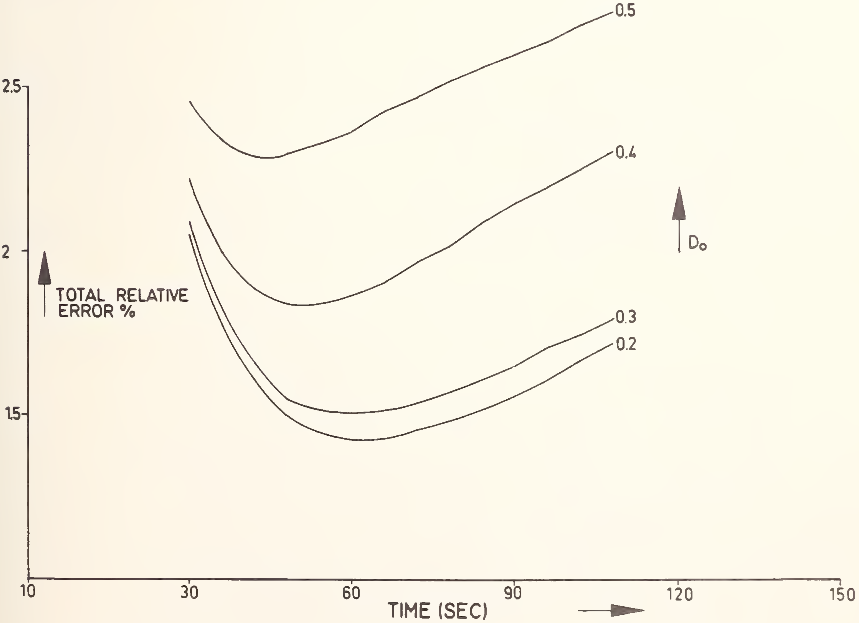

Figure 1. The total relative error in aluminum determinations due to $\overline{\Delta T_m}$ and $\overline{\Delta D_0}$.

sec and waiting time after irradiation, 5 sec. The standard material is $(NH_4) Al (SO_4)_2 \cdot 12 H_2O$ (5.95%). The result for G-2 is 15.47 ±0.08%, in good agreement with the recommended value [3].

III. Determination of Potassium

A. General

The analysis is based upon the measurement of the beta rays of ^{42}K by scintillation counting. The use of a plastic scintillator connected to a one channel analyzer instead of a G.M. tube [4] reduces the influence of dead time and that of ^{24}Na. The detector is mounted in a Perspex castle equipped with slides. The optimal threshold setting is determined experimentally (see Figure 2). The residual gamma-ray count rate of ^{24}Na

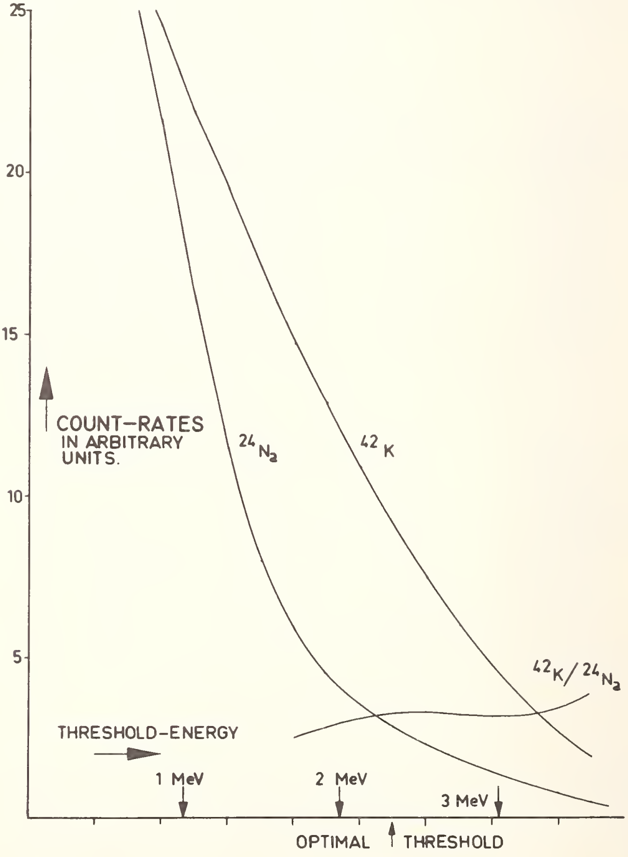

Figure 2. Determination of the optimal threshold setting.

is found by performing a second measurement with a thick Al absorber (1500 mg/cm^2). The distance between absorber and detector is 12 mm. The absorption of the gamma rays of ^{24}Na in the absorber is taken into account.

B. EXPERIMENTAL

Samples are weighed out in small polyethylene containers of 2 mm × 8.3 mm inside diameter. Great care is taken to insure that the containers are completely filled. The amount of sample is 20-30 milligrams, equivalent to 40-60 mg/cm^2. Irradiation time is ten minutes, thermal neutron flux 2×10^{13} n·cm^{-2}·sec^{-1}. Potassium oxalate or phthalate is used as a standard material. After a cooling time of thirty hours, samples and standards are counted with and without the Al absorber. Self-absorption is negligible. Corrections for dead time and gamma-ray absorption are applied. Subtraction gives the true value for the count rate of ^{42}K.

C. RESULTS

The observed count rate is 2×10^4 counts per minute per mg K_2O. The influence of sampling and the value for G-2 are given in Table 5.

Table 5. Results of potassium determinations in some powdered rock samples.

Sample	Way of homogenization of the sample	Average % K_2O	Relative standard deviation Total (%)	Relative standard deviation Between duplicates (%)
Granite I	Quartering	5.72	2.6	0.5
Granite II	Quartering	0.73	1.3	0.9
"	Pouring out the bottle	0.74	3.8	2.2
"	Not homogenized	0.67	5.6	2.0
G−2	Quartering	4.53	2.8	0.8
Granite III	Shaking	5.50	2.7	0.7
Granite IV	Shaking	3.40	2.1	1.2
Granite V	Shaking	6.72	3.6	1.5

Note: Literature data for G−2 as reported by Flanagan [3]: 4.45% K_2O; 4.46% K_2O; 4.5% K_2O; 4.6% K_2O

IV. Determination of Chromium

A. GENERAL

The reaction $^{50}Cr(n,\gamma)^{51}Cr$ provides the most sensitive method for the determination of chromium in silicates. Chemical separation is necessary to eliminate the interference of the ^{233}Th daughter ^{233}Pa and to obtain maximal sensitivity.

B. SEPARATION METHOD

The most convenient separation technique was found to be liquid-liquid extraction of perchromic acid with ethyl acetate. This method was used earlier for spectrophotometric determinations [5,6]. Extraction is quantitative for amounts smaller than 1 mg in the pH region 1.7 ± 0.2.

C. EXPERIMENTAL

After irradiation samples are melted with Na_2O_2 in the presence of carrier. After decomposing the melt with water, filtration and adjustment of the pH the chromate is oxidized with a few drops of a 30% solution of H_2O_2. Extraction is performed two times with 50 ml ethyl acetate previously saturated with H_2O_2. Back extraction (two times) with 10 ml 0.2 *N* NaOH, adjustment of the pH value to 5-6 and precipitation of $BaCrO_4$ leads to a complete separation of chromium. A chemical yield determination is necessary.

D. RESULTS

The count rate in the 0.32 MeV photopeak is 2.8×10^4 counts per min per μg, after irradiating for one week in a thermal neutron flux of 2×10^{13} $n \cdot cm^{-2} \cdot sec^{-1}$ and cooling for two weeks. For G-2 we find an average value of 7.6 ± 0.3 parts per million (ppm) Cr. This is in good agreement with the value of 8 ± 1 ppm reported by Flanagan [3] and that of 7.5 ± 0.1 ppm given by Steinnes [7].

V. Determination of Tin

A. GENERAL

Our method is based upon the reaction:
$^{112}Sn(n,\gamma)^{113}Sn(T_{1/2} = 119\text{ d}) \xrightarrow{\beta^-} {}^{113m}In(T_{1/2} = 102\text{ min})$, although ^{112}Sn has a very low abundance (0.96%). The ^{113m}In activity is isolated and counted using its 0.392 MeV gamma ray (100% abundance) whereas in the usual case of ^{121}Sn beta measurements are necessary [8].

B. SEPARATION METHOD

Samples are melted with Na_2O_2. The melt is dissolved in HNO_3. Tin is coprecipitated with $Fe(OH)_3$. The precipitate is redissolved in 0.3 *N* HF and scandium carrier is added. After one night, precipitation of ScF_3 is complete and the interfering ^{46}Sc is eliminated. A second precipitation of $Fe(OH)_3$ is performed. This is dissolved in 2 *N* HF and the solution is introduced in a small Dowex-2 column (200-400 mesh), mounted in a polyethylene tube. Tin and antimony are absorbed while iron, indium and the alkalies run through. After allowing the equilibrium activity of ^{113m}In to be reached the elution with 2 *N* HF is repeated. To obtain a good counting geometry the indium is readsorbed on a small column of cellulose phosphate in a polyethylene vial which fits into the well of a 3 in. × 3 in. NaI crystal. The gamma-ray spectra of very pure tin and of the separated indium fraction are given in Figures 3 and 4.

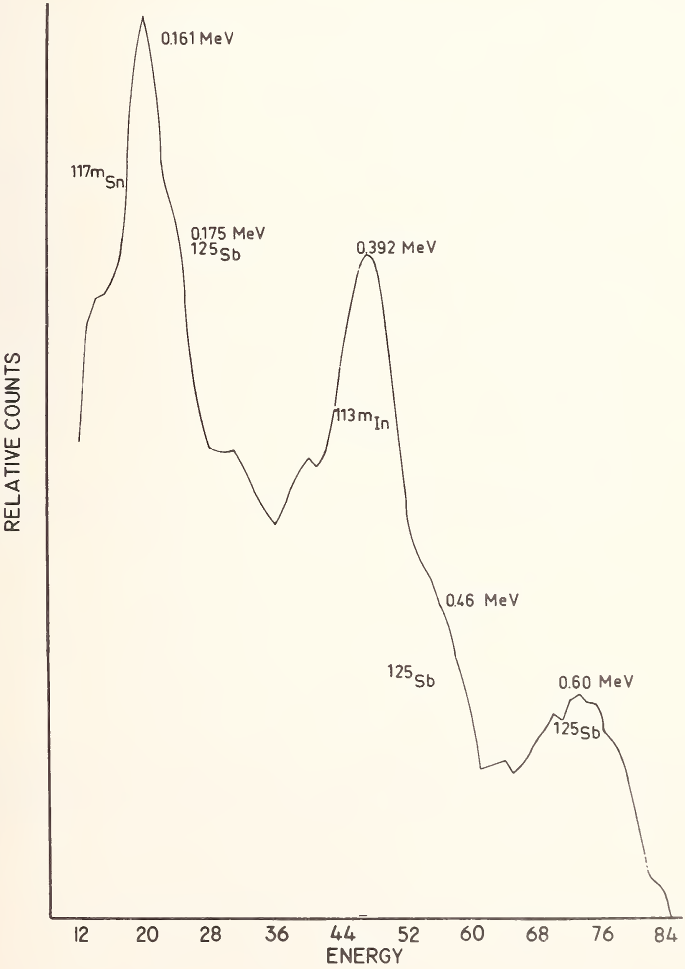

Figure 3. Gamma-ray spectrum of very pure tin metal (6N).

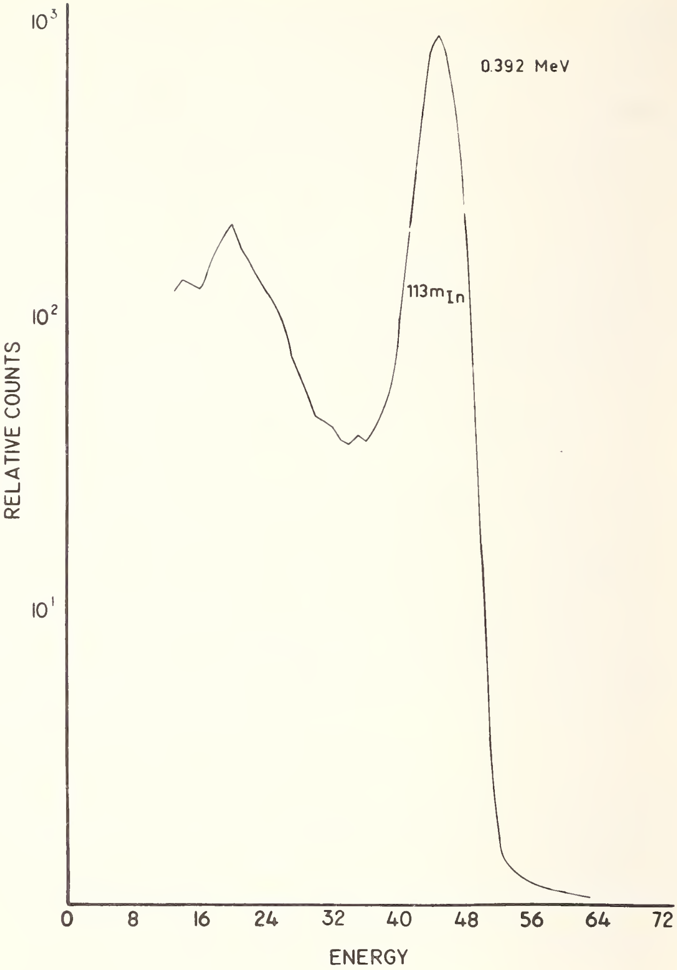

Figure 4. Spectrum of isolated ^{113m}In.

C. Results

The observed specific count rate is 1.7×10^3 counts per minute per microgram of tin. Data for some standard rocks are given in Table 6.

Table 6. The concentration of tin in some standard rocks.

	Our result	Literature value
G–1	3.1 ± 0.1	2–9; 4 recommended
G–2	1.2 ± 0.1	<20; <5; <20
W–1	2.4 ± 0.1	1–3.4; 3 recommended
ACV–1	3 ± 1	<20
PCC–1	0.5 ± 0.2	<20; <9; <20
DTS–1	0.5 ± 0.2	<20; <9; <20
BCR–1	1.5 ± 0.2	<20
CSP–1	4.5 ± 0.5	<20; <10; <20
Mica–Fe (biotite)	65 ± 3	– –
Tonalite T–1	32 ± 3	– –

VI. References

[1] Sijperda, W. S., and Das, H. A., to be published in Beitr. Mineral. Petrogr. **14**, (1968).

[2] Oostrom, M. G., and Das. H. A., to be published in Proc. Koninkl. Nederland Akad. Wetenschap.

[3] Flanagan, F. J., Geochim. et Cosmochim. Acta **31**, 289 (1967).

[4] Winchester, J. W., Anal. Chem. **33**, 1007 (1961).

[5] Brookshier, R. K., and Freund, H., Anal. Chem. **23**, 1110 (1951),

[6] Glasner, A., and Steinberg, M., Anal. Chem. **27**, 2008 (1955).

[7] Steinnes, E., Anal. Chem. **39**, 833 (1967).

[8] Hamaguchi. H., e.a. Geochim. et Cosmochim. Acta **26**, 503 (1962).

DETERMINATION OF TRACE ELEMENTS IN METEORITES BY NEUTRON ACTIVATION ANALYSIS

Wolfgang Kiesl

Analytical Institute of the University of Vienna
A-1090 Vienna, Wahringerstrasse 38

I. Introduction

Based on the development of space research especially with respect to theories about the origin of the solar system and the cosmic abundance of the elements, meteoritic research has gained considerable importance. With the beginning of systematic investigations on meteorites it has been possible to throw some light on the origin and evolution of the planets and the meteorites themselves. However the multiplicity of research has led to innumerable theories which are mainly based on very specialized investigations, the results of which may have possibly been interpreted incorrectly and which therefore had no chance to survive. Nevertheless, explanations for some special problems have been derived. It is my opinion that it will be necessary to coordinate the investigative methods of the various disciplines, *e.g.* astrophysics, mineralogy, petrography, metallurgy, and chemistry (methods of age determination included) to get the very complex picture of the evolution of the planetary system and meteorites.

One of the most important facts in this evolution history is the knowledge of the exact distribution of temperature within the solar nebula before and during the accretion of the primordial dust into planetary bodies. Moreover, it will be very important to have exact knowledge of the chemical composition of the nebula. An important contribution to this point are studies on the chemical composition of planets and meteorites, the latter being performed at our institute.

Our sources of meteorite samples are the Viennese Museum of Natural History, the Mineralogical-Petrographical Institute and the Analytical Institute of the University of Vienna.

Sampling is one of the most difficult problems which is encountered in the chemical analysis of meteorites. This is due to the fact that a meteorite is *a priori* a fraction which has been formed by random partitioning. But I will not discuss these problems here; our methods of sampling are described in detail in a previous paper [1].

At present we are investigating the quantitative determination of about 47 elements in meteorites. About 15 of these elements (namely main constituents and minor elements) are determined by wet-chemical means while the assay of the others is performed using activation analysis and mass spectrometry. For isotopes with half lives exceeding 24 hours an analytical scheme has been developed by our research group for the determination of selenium, arsenic, antimony, tin, rhenium, mercury, osmium, ruthenium, zinc, scandium, gold, iridium, indium, molybdenum, cesium, and rubidium as well as cobalt and chromium which is described in the following chapter.

II. Experimental

For this purpose, about 100-200 mg of each meteorite sample was irradiated together with the standards of the elements to be determined. The irradiation of the samples and standards was carried out in fused containers of quartz. As the source of irradiation the ASTRA-reactor of the Osterreichisch en Studiengesellschaft fur Atomenergie Ges.m.b.H. at Seibersdorf with a neutron flux of $3 \times 10^{13} \mathrm{n \cdot cm^{-2} \cdot sec^{-1}}$ was used. The time of irradiation varied from 60-120 h. After a cooling period of one day, exactly weighed amounts of the meteorite samples were mixed with the corresponding carrier solutions, (we used 5-8 mg amounts of each element) and transferred in a distillation apparatus made of quartz and a hydrogen halide distillation [using a mixture of conc. HCl and 40% HBr (3:1)] was performed. The following elements to be determined were found in the distillate: selenium, arsenic, antimony, tin, mercury, and rhenium, which were separated using an ion exchange resin Dowex 1X8 (100-200 mesh) after the precipitation of selenium by sulfur dioxide. The procedure is described in detail by Kiesl [2].

After this procedure ruthenium and osmium were distilled over from a boiling aqueous solution by adding a concentrated solution of $KBrO_3$. The collecting liquid for the distillate was 2 *N* NaOH. Both elements can be assayed in the presence of each other by gamma spectrometry because their photopeaks are far apart.

After the distillation of osmium and ruthenium, the silicate of the residue was removed, and iron, gold, and molybdenum were continuously extracted with diethyl ether from a 7 *N* HCl solution and separated using an anion exchange resin. (Therefore see flow sheet in Figure 1.)

For further fractionation, the aqueous phase obtained after the ether extraction was poured through an anion exchange column. Iridium, cobalt, zinc, and indium were retained. Using a proper variation of the acidity of the eluent, it was possible to elute cobalt, indium, and zinc whereas the iridium was still adsorbed on the resin. In the 7 *N* hydrochloric acid effluent, it was necessary to separate the large

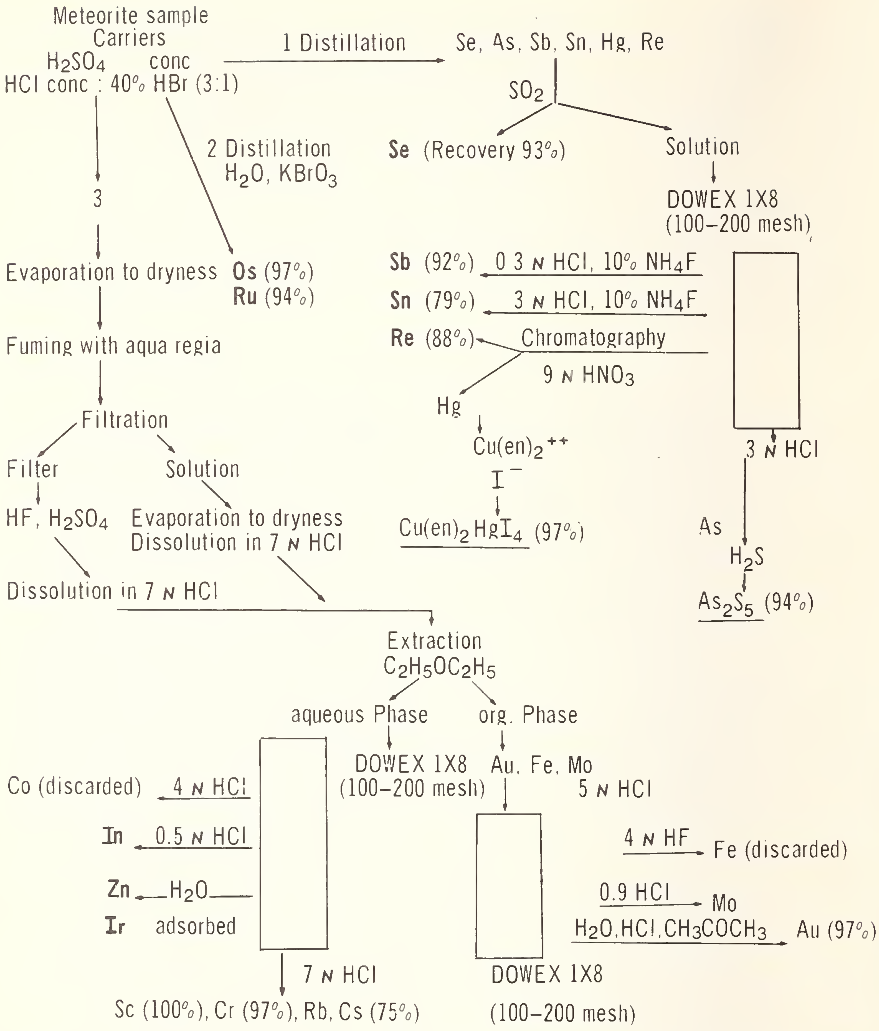

Figure 1. Flow sheet for the separation of trace elements after a long-time neutron activation ($T_{1/2}$ of the nuclides > 24 h).

scandium and chromium activities to be able to detect the rubidium and cesium activities. This was done by firstly precipitating scandium as hydroxide and, secondly, chromium as chromate. In the filtrate the alkalies were finally precipitated as the perchlorates in the presence of ethanol by cooling with ice.

The recoveries were determined radiochemically; the results are shown in the flow sheet in Figure 1.

In Table 1 the isotopes used in this procedure as well as their photopeaks which were evaluated are shown.

Table 1. Nuclides used after the long–time irradiation with thermal neutrons.[a]

	Nuclide	$T_{1/2}$		H (%)	σ (b)	E (μg)	γ (MeV)
Selenium	^{75}Se	120	d	0.87	26	2.6×10^{-2}	0.27
Arsenic	^{76}As	26.7	h	100	5.4	1.5×10^{-4}	0.56
Antimony	^{124}Sb	60	d	42.75	2.5	5.0×10^{-3}	0.60
Tin	^{117m}Sn	14	d	14.3	0.006	0.8	0.16
Rhenium	^{186}Re	90	h	37.07	120	3.0×10^{-5}	0.14
Mercury	^{203}Hg	47	d	29.8	3.8	7.0×10^{-3}	0.28
Osmium	^{191}Os	14.6	d	26.4	40	3.0×10^{-4}	0.14
Ruthenium	^{103}Ru	40	d	31.61	1.44	8.0×10^{-3}	0.50
Gold	^{198}Au	2.7	d	100	96	2.1×10^{-5}	0.41
Molybdenum	^{99}Mo	67	h	23.78	0.51	7.0×10^{-3}	0.14
Chromium	^{51}Cr	27.8	d	4.31	15.9	2.0×10^{-3}	0.32
Scandium	^{46}Sc	85	d	100	12	2.0×10^{-4}	1.12
Cesium	^{134}Cs	2.1	y	100	30	2.0×10^{-3}	0.80
Rubidium	^{86}Rb	18.7	d	72.15	0.91	2.0×10^{-3}	1.08
Cobalt	^{60}Co	5.27	y	100	20	4.0×10^{-3}	1.17
Zinc	^{65}Zn	245	d	48.89	0.47	6.0×10^{-2}	1.12
Indium	^{114m}In	50	d	4.28	56	2.4×10^{-3}	0.19
Iridium	^{192}Ir	74	d	37.30	700	5.0×10^{-5}	0.47

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[a] The sensitivities in μg are calculated for our mean standard conditions.

III. Results and Discussion

In Table 2 the results obtained for a number of olivine-hypersthene chondrites are summarized. The table also contains the values for two carbonaceous chondrites of type II (Mighei) and type III (Grosnaya) respectively.

From Table 2, one can see that certain elements show a depletion in the direction Mighei—Grosnaja—Ordinary chondrites (Se, Zn, In, Cs, Au,

Table 2. Results (calculated to abundance /10^6 Si–atoms) for a number of ordinary chondrites as well as for a type II (Mighei) and type III (Grosnaja) carbonaceous chondrite.

Element	Ordinary Chondrites			Grosnaja	Mighei
	our values[a]		values by others		
Selenium	19.2	(16)	15.0 [3–5]	37.7	62.0
Arsenic	4.3	(16)	4.3 [6]	5.41	4.87
Antimony	0.61	(16)	0.14 [7,8]	0.19	0.208
Tin	<1	(18)	0.64 [9]	2.06	1.37
Rhenium	3.1×10^{-2}	(16)	–	3.60×10^{-2}	3.67×10^{-2}
Mercury	5.50	(16)	1.1 [10]	4.81	4.06
Osmium	0.43	(11)	0.50 [11,12]	0.14_4	0.131
Ruthenium	1.32	(12)	1.40 [12,13]	1.56	–
Gold	0.13	(18)	0.14 [14–16]	0.15	0.15
Molybdenum	2.03	(4)	–	0.90	3.28
Chromium	9.5×10^3	(18)	8.1×10^3 [17]	9.1×10^3	4.96×10^3
Scandium	32.3	(16)	29.6 [18–20]	49.75	21.23
Cesium	5×10^{-2}	(4)	5.3×10^{-2} [21,22]	0.056	0.27
Rubidium	5.0	(6)	5.2 [22–25]	2.37	5.83
Cobalt	1700	(18)	1780 [17]	1890	3644
Zinc	113	(16)	130 [4, 19, 26]	413	587.0
Indium	$<10^{-3}$	(18)	4×10^{-4} [27]	0.067	0.78
Iridium	0.40	(16)	0.35 [14, 28]	0.110	0.22_7

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[a] Numbers in parenthesis show values used.

Sn) whereas the others show little or no depletion. Let me stress now the so-called mercury-paradoxon. Mercury is relatively abundant in ordinary chrondrites. This fact was realized by us in 1966, already, by analyzing the chondrites Mocs and Holbrook [2] and has been confirmed by later analysis of other chondrites. This high abundance of mercury in chondrites and achondrites was confirmed in 1967 by Reed [10] and Ehmann [29]. This paradox, mercury not being depleted as severely as Pb, Bi, Tl, and In, confounds any theory on trace element fractionations. Until now we cannot offer any explanation for this phenomenon either.

Nevertheless, it seems plausible to postulate a high temperature origin for the terrestrial planets and a low temperature formation for the giant planets and the carbonaceous chondrites of type I and II. This can be deduced due to the compositional differences among the planets, the mineralogical investigations on meteorites, and the variation of temperature within the inner regions of the solar system [30].

Our contribution to the solution of the problem of the origin and evolution of the planets and meteorites will deal especially with the necessity to gain knowledge of equilibrium and nonequilibrium conditions by analyzing the distribution of minor and trace elements in the various coexisting phases. Therefrom, conclusions about temperature, pressure, and chemical composition of meteorites, respectively, their parent bodies may be drawn.

IV. References

[1] Kiesl, W., Seitner, H., Kluger, F., and Hecht, F., Monatshefte f. Chemie **98,** 972 (1967).
[2] Kiesl, W., Zeitschrift f. analyt. Chemie **227,** 13 (1967).
[3] Du Fresne, A., Geochim. Cosmochim. Acta **20,** 141 (1960).
[4] Greenland, L. F., *ibid.* **31,** 849 (1965).
[5] Turner, G., J. Geophys. Res. **70,** 5433 (1965).
[6] Onishi, H., and Sandell, E. B., Geochim. Cosmochim. Acta **7,** 1 (1955).
[7] Hamaguchi, H., and Nakai, T., Nippon Kagaku Zasshi **82,** 1485 (1961).
[8] Tanner, I. T., USAEC-Report-2670-75.
[9] Shima, M., Geochim. Cosmochim. Acta **28,** 517 (1964).
[10] Reed, G. W., and Iovanovics, S., J. Geophys. Res. **72,** 2219 (1967).
[11] Morgan, J. W., and Lovering, J. F., Geochim. Cosmochim Acta **31,** 1893 (1967).
[12] Bate, G. L., and Huizenga, J. R., *ibid.* **27,** 345 (1963).
[13] Hara, T., and Sandell, E. B., *ibid.* **21,** 145 (1960).
[14] Baedecker, P. A., and Ehmann, W. D., Geochim. Cosmochim. Acta **29,** 329 (1965).
[15] Vincent, E. A., and Crocket, I. H., *ibid.* **18,** 143 (1960).
[16] Shcherbakov, Yu. G., and Perezhogin, G. A., Geochimistry (USSR) **6,** 489 (1964).
[17] Wood, J. A., The Solar System IV (Ed. Middlehurst and Kuiper) (1963).
[18] Bate, G. L., Potratz, H. A., and Huizenga, J. R., Geochim. Cosmochim. Acta **18,** 101 (1960).
[19] Greenland, L. F., and Lovering, I. V., *ibid.* **29,** 821 (1965).
[20] Kemp, D. M., and Smales, A. A., Analyt. Chim. Acta **23,** 410 (1960).
[21] Gast, P., Geochim. Cosmochim. Acta **19,** 1 (1960).
[22] Smales, A. A., *et al, ibid.* **28,** 209 (1964).
[23] Gast, P., *ibid.* **26,** 927 (1962).
[24] Herzog, L. F., and Pinson, W. H., Am. J. Sci. **254,** 555 (1956).
[25] Murthy, V. R., and Compston, W., J. Geophys. Res. **70,** 5297 (1965).
[26] Nishimura, M., and Sandell, E. B., Geochim. Cosmochim. Acta **28,** 1055 (1964).
[27] Schmitt, R. A., and Smith, R. H., General Atomic Reports GA-6999 and GA-7223 (1966).
[28] Rushbrook, P. R., and Ehmann, W. D., Geochim. Cosmochim. Acta **26,** 649 (1962).
[29] Ehmann, W. D., Geochim. Cosmochim. Acta **31,** 357 (1967).
[30] Kiesl, W., and Hecht, F., Paper presented at the "International Symposium on Meteorite Research" IAEA-Vienna, August 1968.

THE NONDESTRUCTIVE DETERMINATION OF IRIDIUM IN METEORITES USING GAMMA-GAMMA COINCIDENCE SPECTROMETRY

W. D. Ehmann and D. M. McKown

Department of Chemistry
University of Kentucky
Lexington, Kentucky 40506

I. Introduction

Much work has been directed toward obtaining accurate Ir abundances in meteoritic materials by several techniques of activation analysis [1-3]. However, the results of various workers bear considerable differences. Among the factors believed responsible for these deviations are (a) the difficulty of dissolving completely, Ir aggregates if such exist in meteorite metal phases, (b) difficulty in equilibrating the oxidation states of the dissolved active Ir and the added carrier, and (c) the unpredictable chemistry of multivalent elements in general. The validity of the Ir data has, in some cases, been left to question since there has been no real basis for evaluating these possible errors.

A nondestructive procedure for the determination of Ir in meteorites containing at least 0.1 parts per million (ppm) Ir has been developed utilizing neutron activation followed by gamma-gamma coincidence spectrometry. The procedure eliminates problems associated with the radiochemical separation of Ir. Errors due to preirradiation contamination, irradiation variables, and the coincidence counting arrangement must be evaluated, however, in order to establish validity of such data. This nondestructive technique may then be used to evaluate the various chemical procedures previously employed.

II. Experimental

A. The Coincidence Counting System

The block diagram of the system used in this work is shown in Figure 1. The system consists of two 3 in. × 3 in. NaI(Tl) detectors coupled to photomultiplier tubes with voltage divider networks specially designed to reduce the gain shifts of the detector assemblies, two double delay line amplifiers, two jitter-free single channel analyzers, a fast coincidence module, and a 400 channel analyzer with a slow coincidence input gate [4]. The multichannel analyzer input pulse is taken through a variable delay line from one of the detector outputs. In the present work the system has been kept as simple as possible and was designed to give desirable parameters for application to specific activation analysis problems. The total detector-coincidence system was checked to determine the effects of long-term drift, short-term gain shifts, and dead time variations on the reproducibility of coincidence count rates. The short-term variations are less than ±5 percent of the average coincidence count rate, long-term drift is less than 2 percent, and only very small dead time shifts occur under counting conditions encountered in this study.

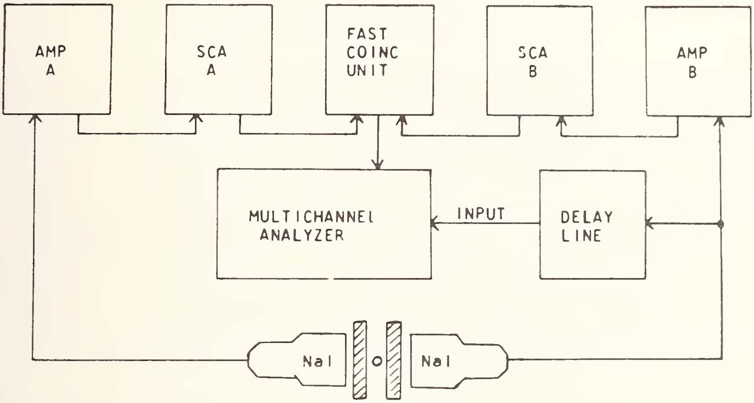

Figure 1. Block diagram of the coincidence counting system.

In order to determine the precision and accuracy of quantitative activation analysis data derived from this counting system utilizing precise time and energy discrimination, a more or less ideal test case was selected. Standard rock samples and sodium standards were irradiated for 1 hour in a thermal flux of 10^{12}n·cm^{-2}·sec^{-1} and the energy region from approximately 1 to 2 MeV counted in coincidence with the 2.75 MeV gamma-ray of ^{24}Na. These peaks predominate in the gross spectra of most the samples. The gating single channel analyzer window was carefully adjusted so that a maximum energy shift of ±5% would exclude a portion of the 2.75 MeV gamma-ray distribution causing large count rate changes. Each sample was counted 4 times and approximately 10,000 counts were accumulated during each counting interval. Table 1 lists the calculated Na_2O abundances together with the counting precision and recommended values. These and similar data for Sc, La, and Co illustrate that reliable quantitative data can be obtained using this system.

Table 1. Sodium abundances in some standard rocks.

Rock samples	Average % Na_2O	Reported value(s)[a]
GH	3.78 ± .11	3.83
GR	3.39 ± .14	3.80
SUL – 1	0.95 ± .04	0.91
SYE – 1	2.80 ± .05	2.74; 2.94; 3.29

[a] Sciences de la Terra, XI, 105 – 121 (1966).

B. DETERMINATION OF IRIDIUM

Iridium-192 formed by the reaction $^{191}Ir(n,\gamma)^{192}Ir$ decays *via* cascade gamma emission [5]. The feasibility of the nondestructive method for Ir in meteorites depends on the specificity afforded by coincidence spectrometry, the extremely large thermal neutron capture cross section of ^{191}Ir(700b), and the fact that the ^{192}Ir produced is long-lived (H=74 days). The long half life permits determination of Ir after the decay of high initial activity radionuclides produced from the more abundant elements.

The powdered meteorite samples to be assayed (100-200 mg) were weighed into polyethylene vials and later heat-sealed [6]. Iridium flux monitor samples were prepared by evaporating a standard Ir solution onto finely ground SiO_2 in similar vials. The samples and flux monitors were irradiated together for 1 hour in a thermal neutron flux of $5 \times 10^{12} n \cdot cm^{-2} \cdot sec^{-1}$ using the "rabbit" position at the Air Force Reactor (AFNETF), Dayton, Ohio. The samples were counted after a decay period of approximately 2 weeks.

The gross singles spectrum of a meteorite is shown in Figure 2. The ^{192}Ir photopeaks (approximately 0.32, 0.47, 0.6 MeV) are completely disguised by the presence of ^{51}Cr, annihilation radiation, and the Compton spectrum of higher energy activities. Figure 3 shows the coincidence spectra obtained for this meteorite sample and an Ir flux monitor. Those events in region B (Fig. 2) were counted in coincidence with those of region A. The integrated activity of the 0.32 MeV peak was used for the abundance calculation because the 0.47 MeV peak contains contributions from annihilation coincidences due to the overlap of channel A into the 0.51 MeV region.

Attempts made thus far to confirm the validity of the nondestructive results consist of (a) standard addition of other radionuclides known to be present, (b) iridium peak ratio studies, (c) comparison of results obtained using different gating window settings and resolution times, and (d)

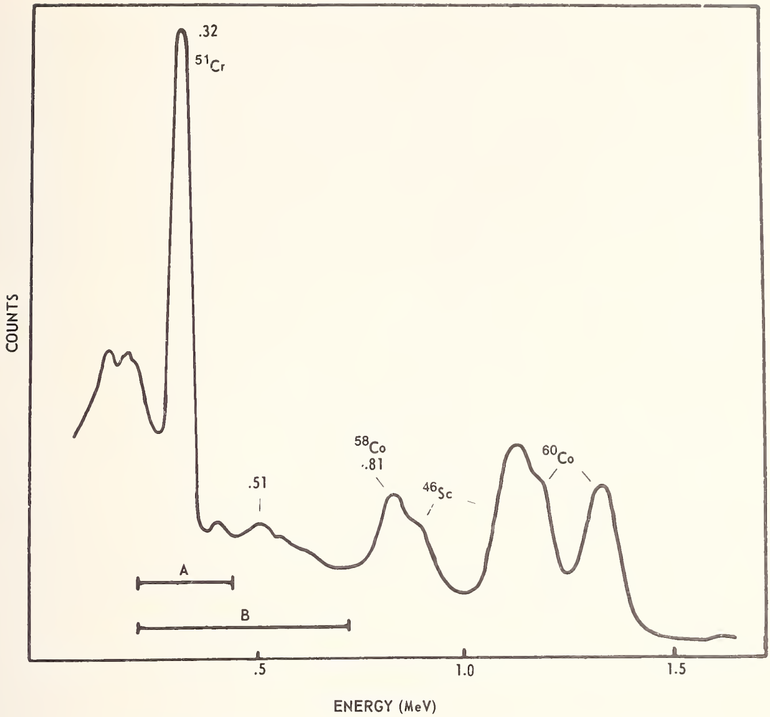

Figure 2. Gamma-ray spectrum of an irradiated meteorite.

comparison of sample and standard half lives. In addition, irradiation positional analysis and self-shadowing experiments were carried out. The deviation of an individual flux monitor specific activity from the average flux monitor specific activity was never greater than 5% over the entire irradiation unit (size 2 in. × 1/2 in. diameter).

III. Results and Discussion

The very high ^{51}Cr activity (0.32 MeV) found in irradiated meteorites can be eliminated even at coincidence resolution times a factor of 2 or 3 longer than that used in these determinations. Experiments employing ^{51}Cr addition confirm that chance coincidences from this radionuclide do not contribute significantly. Standard addition of other radionuclides which decay by gamma-cascade, for example ^{60}Co, ^{46}Sc, and ^{58}Co, were also carried out. The Compton coincidences from these isotopes add to the coincidence spectra background activity, but the baseline corrected activity of the 0.32 MeV peak remained the same within the precision previously indicated.

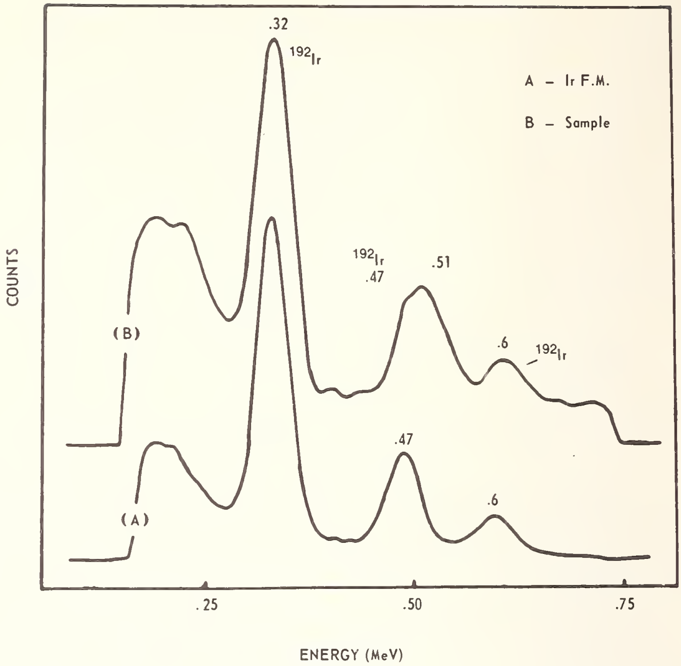

Figure 3. Gamma-gamma coincidence spectra of (A) Ir flux monitor and (B) irradiated meteorite.

The attempts to do iridium photopeak area ratio studies were limited by the fact that the 0.6 MeV peak is not well defined in the coincidence spectrum except for those samples of very high Ir content. For high activity samples, however, the 0.6 MeV/0.32 MeV peak area ratio compares favorably with the Ir standard spectra. As indicated in Figure 3 (B), the 0.47 MeV peak of ^{192}Ir can be partially resolved. The baseline corrected peak height ratio 0.32 MeV/0.47 MeV (shoulder) agreed within 10% with that for the Ir standard spectrum. In addition, the ^{192}Ir peaks for some of the samples could be resolved from contaminating activities to a fair degree using a Ge(Li) detector. These results also confirm that the 0.32 MeV coincidence peak is without significant interference. Results obtained using several different gate window settings and resolving times are in good agreement.

Some of the data obtained for Ir in meteorites are summarized in Table 2. A comparison is made between the coincidence results and those obtained using a Ge(Li) detector. Also compared are coincidence results obtained using two different gate window settings and the results of other workers. It should be mentioned that the chemical methods used to standardize the iridium flux monitor solution are also subject to the analytical difficulties previously mentioned. The flux monitor solution used in these experiments was standardized by isotope dilution analysis using two different procedures (a) direct hydrogen reduction of the evaporated chloride solution ($IrCl_3$ in HCl) residue and (b) hydrogen reduction of the chemically separated hydrous oxide. The results of the two procedures differed by less than 10%. Work is now in progress which will remove this uncertainty by preparing standard solutions directly from iridium metal *via* alternating current dissolution [7].

Table 2. Comparison of iridium abundance results (ppm).

	Coincidence gate setting			
Sample	(.32 MeV)	(.47 and .6 MeV)	Ge (Li)	Other workers
Harleton	0.50	0.47		0.45[a]
Ochansk	0.81	0.77		0.51[a]
Forest City	0.83	0.81		0.50[a], 0.57[a]
Murray	0.59		0.57	0.38[a]
Abee	0.55		0.50	0.083[a], 0.32[b]
Atlanta	0.60		0.62	0.18[a]
Plainview	0.66			0.47[a], 0.50[a]
Orgueil	0.65			0.36[a], 0.42[b]
Saratov	0.57			

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[a] Geochim. Cosmochim. Acta 29, 329–42 (1965).

[b] Reference [3].

Since absolute half life determination from coincidence spectra is difficult, the calculated Ir abundances with increasing decay time were compared. The calculated Ir content of a single Murray meteorite sample after decay of 10, 34, 54, and 120 days was observed to be 0.59, 0.59, 0.62, and 0.54 ppm, respectively. The observed Ir content of the Abee meteorite for the above decay times was 0.55, 0.53, 0.55, and 0.61 ppm, respectively.

All 0.32 MeV peak identification tests indicate that this peak is due to ^{192}Ir alone. Any interference would have to have approximately the same life-time as the Ir isotope. Due to the short irradiation time used, significant interference could only be produced from an element of major abundance in meteorites or one with a very large thermal capture cross section. A search in tabulations of nuclear data yielded no radionuclides that could be produced in meteorites by thermal neutron irradiation which fill these prerequisities and have the same coincidence counting efficiency as ^{192}Ir for the different gate window settings used.

IV. Acknowledgments

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V. References

[1] Baedecker, P. A., Ph.D. Thesis, University of Kentucky, U.S.A.E.C. Document No. ORO-2670-17, 1967.
[2] Barker, J. L., Jr., and Anders, E., Geochim. Cosmochim. Acta **32,** 627-45 (1968).
[3] Crocket, J. H., Keays, R. R., and Hsieh, S., Geochim. Cosmochim. Acta **31,** 1615-23 (1967).
[4] Vogt, J. R., Ph.D. Thesis, University of Kentucky, U.S.A.E.C. Document No. ORO-2670-10, 1966.
[5] Lederer, C. M., Hollander, J. M., and Perlman, I., Table of Isotopes, John Wiley and Sons, New York, 1967, p. 372.
[6] Ehmann, W. D., and McKown, D. M., Anal. Chem. **40,** 1758-59 (1968).
[7] Butler, T. A., comp., Oak Ridge Isotopes Development Center Progress Report, U.S.A.E.C. Document No. ORNL-TM-530 (Rev.), 1962.

DETERMINATION OF SOME RARE EARTHS IN ROCKS AND MINERALS BY NEUTRON ACTIVATION AND GAMMA-GAMMA COINCIDENCE SPECTROMETRY

O. B. Michelsen and E. Steinnes

Institutt for Atomenergi
Kjeller, Norway

I. Introduction

Although gamma-gamma coincidence measurements represent a comparatively specific system for the determination of certain components in complex radionuclide mixtures, this technique has not been extensively used in activation analysis. The main reason for this is probably the relatively low counting efficiency obtained in this type of measurement.

In connection with an investigation of potential sources of rare earth elements in Norway the need arose for simple and accurate methods for the determination of these elements in a great number of samples, mainly rocks and minerals. Besides more conventional techniques, such as x-ray fluorescence spectrometry, atomic absorption spectrometry, and direct neutron activation analysis, it was also decided to try gamma-gamma coincidence spectrometry following neutron activation of the samples.

Several rare earth elements produce isotopes emitting gamma-gamma coincident radiation by neutron activation (La, Ce, Nd, Sm, Eu, Tb, Dy, Er, Yb, Lu). In this work we have primarily concentrated on Eu, first because it proved difficult to determine in the actual samples by other instrumental techniques, and second because this element is in the focus of interest for commercial reasons. A routine method for the determination of Eu, based on the 9.3 h ^{152m}Eu is presented. Measurements based on the 12 y ^{152}Eu have also been tried with satisfactory results. In addition preliminary experiments on the determination of La, Sm, Tb, Yb, and Lu are described.

II. Experimental

A. Counting Equipment

The detectors used were Harshaw integral line detectors with 2 in. × 2 in. NaI(Tl) crystals. They were mounted on a rack which made it possible to change the angle between the central axes of the detectors continuously in the range 90 to 180 degrees. The detectors were connected *via* Hamner charge sensitive amplifiers to a Hamner coincidence unit consisting of 2 linear double delay line amplifiers, 2 jitter-free pulse-height analyzers and a fast coincidence unit. The output of the latter was used to gate a Tullamore 400-channel pulse-height analyzer. During measurements the distance between the detectors and the sample was so adjusted that the dead time of the multi-channel analyzer in no case exceeded 40 percent when the pulses from either detector were fed *via* the preamplifier directly into the analyzer.

B. IRRADIATION

10 mg samples, weighed into flat polyethylene bags, were used. As standards were used aliquots of dilute solutions, evaporated to dryness. Irradiations were performed at a flux of $1.5 \times 10^{13} \mathrm{n \cdot cm^{-2} \cdot sec^{-1}}$ in the reactor JEEP-2. Thee samples were stored for appropriate times before activity measurements. The following irradiation times were applied for the various elements: Eu (9.3h), Sm, La (15 min), Eu (12 y), Tb, Yb, Lu (1 d).

C. DETERMINATION OF EU *via* THE 9.3 H ^{152m}EU

The measurements were carried out 20-28 h after the irradiation. Various coincidences were tested. The 122 keV-840 keV coincidence was selected because the interference from other elements was found to be less pronounced in this case. Angular correlation measurements showed that maximum intensity was obtained at an angle of 90° between the detector axes. As gate was used the 122 keV peak, and accordingly the 840 keV peak made the basis for the numerical evaluation of the spectra. Time of measurement was usually 10 min, in some cases up to 30 min. Interference with this coincidence from other RE (La, Sm, Tb, Ho, Yb, Lu) was tested 24 h after a 15 min irradiation and was found to be <0.03 percent at equal amounts of elements. A similar investigation of possible interferences from ^{56}Mn and ^{72}Ga which are the most probable contributors to a complex 0.84 MeV photopeak in most irradiated rocks proved the interference to be 0.015% percent and 0.2% percent, respectively. This method is now routinely used for Eu determinations in the concentration range 10-100 parts per million (ppm) of Eu.

D. DETERMINATION OF EU *via* THE 12 Y ^{152}EU

Some preliminary experiments to test this possibility have been performed. Various coincidences have been compared. The 344 keV-779 keV coincidence was chosen because of few interferences, both from other gamma rays of ^{152}Eu and from other long-lived nuclides (^{160}Tb, ^{233}Pa, ^{59}Fe, ^{46}Sc *etc.*). After 3 weeks storage after irradiation, the samples were measured for 10 minutes. The gate was placed over the 344 keV peak, and the measurements were based on the 779 keV gamma ray.

E. DETERMINATION OF LA AND SM

Determinations of these elements have been performed after a storage time of 5 days. The determination of La through the 490-1590 keV coincidence of ^{140}La proved to be very satisfactory. In most of the samples, however, the content of La was high enough to permit equally good determination by means of the 1590 keV gamma ray in singles spectrometry.

Sm has been determined by gating with the 41 keV x-ray of ^{153}Sm and measuring the 103 keV gamma ray. (Most of the x-rays emitted originate from internal conversion of the 70 keV gamma ray, which is coincident with the gamma ray of 103 keV). By this means less interference from other RE nuclides and ^{233}Pa is encountered than by corresponding singles spectrometric measurements.

F. DETERMINATION OF TB, YB, LU

Determination of these elements have been attempted after 2 weeks delay. Various coincidences of ^{160}Tb were tested. The alternative less subjected to spectral interference was found to be gating over the 880 keV-970 keV photopeaks and measuring the 298 keV peak which is in coincidence with both. A 30 min measurement time was used. The determination of Yb and Lu through their respective isotopes ^{169}Yb and ^{177}Lu was found to be difficult mainly owing to mutual interference.

G. TEST SAMPLES

Three different apatites and one iron ore sample were selected for testing the methods. These samples have a total RE content of the order of 1 percent, and were considered representative of the type of samples to be analyzed on a routine basis.

H. SHIELDING EFFECTS

As some RE elements (Sm, Eu, Gd) are strong neutron absorbers the results may be subjected to errors associated with shielding effects. The following experiments were carried out to study this point:

1. The test samples were analyzed for Sm, Eu and Dy, partly by analysis of the solid samples, and partly by analysis of their solutions. The method employed for this was singles gamma spectrometry in the manner

described in a previous work [1]. No significant difference between the results was observed, indicating that shielding effects were of minor importance in the concentration range covered by the test samples, and hence, should not influence the results obtained for the actual samples.

2. The self-shielding effect of Eu was studied by adding known amounts of Eu to a rock sample containing about 40 ppm of Eu. The Eu was added in increments of 50 ppm up to a maximum of 200 ppm, and the total content of Eu was determined by the coincidence method for each addition. Plots made of the total Eu concentration as a function of the added amount gave a straight line which was extrapolated to zero addition. It was found that the self-shielding effect of Eu could be neglected in the range studied.

III. Results and Discussion

A. RESULTS

In Table 1 are shown some results of Eu determination made on the test samples. A few terbium results are also included. The Eu results obtained by the different isomers of ^{152}Eu are in good agreement which also apply to results obtained using the singles spectrometry method [1]. The precision of the results available for evaluation so far is about 5 percent.

B. DISCUSSION

Gamma-gamma coincidence measurements of the 9.3 h ^{152m}Eu resulting from neutron activation have proved to be a convenient method for the determination of Eu in large series of rock samples. Work on similar methods for some of the other RE is in progress. These methods will perhaps be particularly useful as methods for checking other analytical techniques for determining RE.

One problem when applying coincidence counting techniques is the low intensity obtained. This is particularly unfavorable since the total amount of radiation entering the detectors is not reduced. To achieve this attempts are being made to use lead absorbers where possible, in order to prevent radiation of energies lower than those involved in the actual measurement from contributing to the background. This means that the detectors may be placed closer to the samples.

It is possible to determine all the elements considered in this work by means of Ge(Li) detectors. We have also tried to do this, but the lack of stability of the detectors available to us so far has, however, excluded their use as instruments for routine analysis of large series of samples.

Table 1. Europium and terbium contents of four test samples (ppm).

Element	Kodal apatite	Karlshus apatite	Ødegaarden apatite	Iron ore
Europium	57.7	12.6	50.3	50.8
	55.8	13.2	49.3	56.3
(9.3 h ^{152m}Eu)	58.6	12.0	46.9	50.5
	61.0	12.1	50.5	52.6
	53.3	12.4	43.5	57.9
	60.3	13.9	47.0	59.1
	57.2	14.2	48.9	52.4
	55.2	12.5	47.2	50.8
	58.8	13.6	45.8	52.1
	53.9	12.8	47.6	51.0
Mean	57.2	12.9	47.7	53.4
Europium	57.6		47.8	45.7
	58.1		52.3	49.2
(12 y ^{152}Eu)	58.3		48.1	49.6
	59.9		51.9	51.1
	62.3		50.5	52.0
Mean	59.2		50.1	49.5
Europium, singles NaI spectrometry	64	13	50	52
Terbium	26.0	84.4	97.9	
	21.5	85.8	96.7	<1.4
(72 d ^{160}Tb)	20.1	82.5	85.9	
	23.3	86.1	92.8	
	22.8	83.3	91.3	
Mean	22.7	84.4	92.9	<1.4

IV. References

[1] Steinnes, E., Report KR-120, Kjeller, Norway (1967).

NEUTRON ACTIVATION METHOD FOR THE ISOTOPIC ANALYSIS OF LEAD

P. P. Parekh, M. Sankar Das and V. T. Athavale

Analytical Division
Bhabha Atomic Research Centre
Trombay, Bombay-74, India

I. Introduction

Neutron activation analysis has come to stay as a sensitive and specific method of elemental analysis at trace concentration.

In principle for a poly-isotopic element it is also a method of determining one or more isotopes of this element [1]. In Table 1 is listed the studies in which this technique has been employed for the isotopic analysis of elements. The limited interest in this method as an "isotope-analyzer" arises presumably because solid source mass spectrometry gives a higher precision, requires less sample for analysis, and is an absolute method for the measurement of isotopic ratios.

The work of Seyfang [3] on the isotopic analysis of uranium suggests that if the various factors that spoil the precision of this otherwise sound

Table 1. Isotopic analysis using neutron activation method.

Isotope analyzed	Nuclear reaction employed	Field of study	Reference
Uranium–235	(n, f)	Analytical	Seyfang and Smales [2] Seyfang [3]
Argon–40	(n, γ)	Geochronology	Moljk et al. [4] Stoenner and Zahringer [5] Herr [6] Armstrong [7]
Rhenium–187	(n, γ)	Geochronology	Herr [6]
Osmium–184, 190, 192	(n, γ)		Hirt et al. [8]
Manganese–53	(n, γ)	Meteoritics	Herper et al. [10]
Scandium–45	(n, γ)		
Calcium–48	(n, γ)	–––	Corless and Winchester [11]

method are critically evaluated, it should be possible to achieve a high degree of precision. As regards the sample requirements, there are areas of applications such as the isotopic analysis of lead in galenas where serious limitation in the availability of samples does not exist.

Analysis of total lead in meteorites using the nuclear reactions on lead-204 and lead-208 has been reported by Reed and co-workers [12]. A previous communication from this laboratory reported the use of fast and thermal reactor neutron activation on lead-204 and lead-208 for the dating of thorium minerals [9].

The present paper describes the studies carried out to evaluate the attainable precision in the analysis of lead-208 to lead-204 ratio with a view to determine the "model ages" of galenas.

II. Experimental

A. Apparatus and Reagents

All the reagents used in this work were of recognized analytical purity.

1. Standard Lead

Since a number of repeated runs were contemplated in order to assess the attainable precision in the determination of lead-208 to lead-204 ratio, it was necessary to have a sufficient quantity of the standard. Hence, a sample of BDH AnalaR lead-nitrate was converted to lead tetramethyl and analyzed for its isotopic composition by means of a CEC mass spectrometer type 21-110B. Lead was found to have the normal isotopic composition of 1.475% lead-204, 23.6% lead-206, 22.6% lead-207 and 52.3% lead-208 and was used as a reference.

2. Counters

The β^- activity of the samples was counted by means of an end window (aluminized Mylar window, 0.9 mg/cm^2 thick), gas flow β^- proportional counter (I-1350) type PCS14B fabricated by the Electronics Division, Bhabha Atomic Research Centre, Trombay.

The gamma activity measurements were made with a 3 in. × 3 in. NaI(Tl) crystal connected to a single channel analyzer type Medical Spectrometer RD 322 fabricated by Nuclear Instruments and Systems Section, Bhabha Atomic Research Centre, Trombay.

The stability of the beta and gamma counters were checked by means of standard U_3O_8 (>1 year old) and cobalt-60 sources, respectively. The variations observed in the counting rates of these sources from time to time were found to be well within the statistics of counting.

3. *Procedure*

a. Preirradiation treatment: Galenas were dissolved in nitric acid, purified by two crystallizations from fuming nitric acid (80-85% nitric acid concentration), dissolved in deionized water and evaporated to dryness. The dried crystals were crushed to a fine powder for an easy encapsulation.

b. Irradiation details: The standard and a sample were closely packed in 2 mm to 3 mm diameter polyethylene capsules, heat sealed, and were then placed in close proximity inside a push-fit polyethylene vial, sealed with Araldite and irradiated in the Al position of "Aspara" for a 6-hour period.

Sample and standard irradiated at CIRUS were covered in separate foils of high purity aluminum, wrapped together in an aluminum foil and irradiated in one of the self-serve positions for 4 days and cooled overnight.

c. Postirradiation treatment: The postirradiation treatment consisted of crystallization as lead nitrate from fuming nitric acid twice, followed by precipitation as $PbCl_2$ twice and a final separation as $PbSO_4$. The lead sulphate precipitate was dissolved in 15% (W/V) hot ammonium acetate and then precipitated as chromate at a pH of 5 to 6 [13].

Lead chromate was filtered hot, washed thrice with hot water and finally with absolute alcohol, dried at 120 °C for 10 min, cooled and weighed as $PbCrO_4$.

In the case of samples irradiated at CIRUS with a relatively higher thermal flux and longer irradiation periods, the procedure given above was not found to be adequate for obtaining radiochemically pure lead activities.

Hence, after the second precipitation of lead chloride, it was dissolved in hot 1.5 *M* HCl, adsorbed on an anion exchanger IRA-400, followed by elution with hot water. The rest of the procedure was the same as described above.

III. Results

The overall precision of the method was evaluated with the help of a reference sample. Table 2 gives the ratio of the observed specific activities of lead-209 and lead-204m calculated on the basis of seven runs of the reference sample. In each run two splits of the sample were irradiated simultaneously, one of them being treated as an unknown sample.

The accuracy of the method was evaluated by determining the isotopic ratio of lead-208 to lead-204 on an inter-laboratory standard galena, T-1003, and comparing it with the mass spectrometric values reported by different laboratories. These results are tabulated in Table 3. The

Table 2. Evaluation of the overall precision of the method.

Run No.	Ratio of specific activity of Pb–209 A	Ratio of specific activity of Pb–204m B	A/B (mean value)
1	0.998	0.991	
2	1.00	1.008	
3	1.012	1.007	
4	0.990	0.981	0.999 ± 0.014
5	0.988	1.002	(1σ)
6	1.011	1.001	
7	0.992	1.008	
Mean	0.999 ± 0.010 (1σ)	1.000 ± 0.012 (1σ)	

Table 3. Evaluation of the accuracy of the method.

Sample No.	Present work			Other work [14, 15]
	% Pb–208	% Pb–204	$\frac{\text{Pb–208}}{\text{Pb–204}}$	$\frac{\text{Pb–208}}{\text{Pb–204}}$
T–1003	52.31 ± 0.45	1.462 ± 0.012	35.78 ± 0.42	a) 35.64 b) 35.87 c) 35.93 d) 35.76 e) 35.80 ± 0.08 f) 35.70 ± 0.18 g) 36.03 h) 36.05 i) 35.99
ChGR	52.82 ± 0.19	1.573 ± 0.01	33.69 ± 0.24	33.43

available mass spectrometric data on galena from Chitaldrug (sample ChGR) has also been included here for comparison.

The model-ages of a few galenas were determined from their lead-208/lead-204 values and are given in Table 4.

IV. Discussions

In order to achieve high precision in the analysis the weights of the sample and standard were adjusted such that the recorded activity in a 2

Table 4. Model–age of galenas.

Sample No.	Locality		$^{208}Pb/^{204}Pb$	Model age[a] (in million years)
T–1003	Broken Hills, Australia		35.73 35.80 35.82	1591 1559 1550
		Mean	35.78 ± 0.42	1567 ± 192
ChGR	Chitaldrug, Mysore State		33.88 33.78 33.52 33.50	2413 2457 2569 2578
		Mean	33.69 ± 0.24	2504 ± 104
BGA	Bellary, Mysore State		35.82 35.44	1547 1718
		Mean	35.63	1632
———	? (Bhander Series)		37.55 36.91	741 1046
		Mean	37.23	893
BAGA	Baroda, Gujarat State		38.90 39.15 38.98	98 –25 (?) 59
		Mean	39.01	78[b]
DGA	Dhone, Andhra Pradesh		50.28 51.06 50.64	'J' type
		Mean	50.66	
DKGA	Devarakonda, Andhra Pradesh		53.91 54.09 53.02 53.71	'J' type
		Mean	53.91	

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[a] Calculated on the 'Russel–Farquhar–Cumming' Model.

[b] Negative age–value was rejected in the calculation of the mean–age.

min period was between 50,000 and 100,000 counts so that the errors from counting statistics were lower than 0.44%. To minimize the errors from self-absorption in the β-counting of lead-209, the weights of the standard and the sample were adjusted to lie between 5 to 6 mg/cm². The errors in weighing were estimated to be less than 0.3%. From the data given in Table 2, the overall precision of the analysis of the isotope ratio lead-208/lead-204 can be calculated to be of the order of 1.4%. The results given in Table 3 indicate satisfactory accuracy in the determination of the lead-208 to lead-204 ratio.

The precision obtained in the present study is poorer by a factor of about 2 to 3 as compared to some of the typical values reported by mass spectrometry [14]. It is however felt that the method is quite capable of establishing geological age-patterns. Better precision could be achieved if a number of splits from a given sample were irradiated and processed together, but this approach is difficult in view of the comparatively short half life of the nuclides lead-204m ($T_{1/2} = 67$ min) and lead-209 ($T_{1/2} = 3.3$ h) involved in the study. This difficulty could be obviated to a great extent by using lead-203 ($T_{1/2} = 52$ h) formed by the lead-204 (n,2n) lead-203 reaction. However, the induced saturation activity of this nuclide is lower by a factor of four [16-18].

V. Acknowledgments

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VI. References

[1] Mapper, D., Methods in Geochemistry, Smales, A. A., and Wager, L. R., Eds., Interscience Publishers Ltd., 1960, p. 299.

[2] Seyfang, A. P., and Smales, A. A., Analyst **78**, 394 (1953).

[3] Seyfang, A. P., ibid **80**, 74 (1955).

[4] Moljk, A. R., Drever, R. W. O., and Curran, S. C., Nucleonics **13**, 44 (1955).

[5] Stoenner, R. W., and Zahringer, J., Geochim. Cosmochim. Acta **15**, 40 (1958).

[6] Herr, W., Proc. of Radioactivation Analysis Symposium, I.A.E.A., Butterworths, London, 1960, pp. 35-52.

[7] Armstrong, R. L., Geochim. Cosmochim. Acta **30**, 565 (1966).

[8] Hirt, B., Herr, W., and Hoffmeister, W., Proc. of Symposium on Radioactive Dating, I.A.E.A. Vienna, 1963, pp. 35-43.

[9] Athavale, V. T., and Parekh, P. P., Proc. on Nuclear and Radiation Chemistry Symposium, Waltair, 1966, p. 200.

[10] Herpers, U., Herr, W., and Wolfe, R., Proc. of Symposium on Radioactive Dating and Methods of Low-level Counting, I.A.E.A., Vienna, 1967, pp. 199-205.

[11] Guinn, V. P., Advances in Neutron Activation Analysis, Progress in Nuclear Energy Series IX, Analytical Chemistry, Pergamon Press, New York, 1966, p. 86.

[12] Reed, G. W., Kigoshi, K., and Turkevich, A., Proc. 2nd Int. Conf. P.U.A.E., Geneva **28**, p. 953 (1958).
[13] Vogel, A. I., Quantitative Inorganic Analysis, Longmans Green & Co., Ltd., London, 1960, pp. 420-21.
[14] Russel, R. D., and Farquhar, R. M., Lead Isotopes in Geology, Interscience Publisher Inc., New York, 1960, pp. 22 and 172.
[15] Doe, B. R., J. Geoph. Res. **67**, 2900 (1962).
[16] Roy, J. C., and Hawton, J. J., AECL-1181 (1960).
[17] Durham, R. W., Navalkar, M. P., and Ricci, E., AECL-1434 (1962).
[18] Parekh, P. P., Sankar Das, M., and Athavale, V. T., unpublished work.

DETERMINATION OF PROTACTINIUM BY NEUTRON ACTIVATION AND ALPHA SPECTROMETRY[1]

J. N. Rosholt and B. J. Szabo

U.S. Geological Survey
Denver, Colorado 80225

I. Introduction

Stable and radioactive daughter products from uranium decay have proved useful in fundamental studies of the geochemistry of uranium in igneous rock and sedimentary environments and in ore deposits. Information gained from geochemical studies of uranium migration have been used to develop models for attempts to date archaeological, geological, and oceanographic environments represented by samples of bone, wood, charcoal, continental and marine carbonates, marine sediments, and glacial-derived soils.

The decay series of uranium and thorium down to the radium isotopes are shown in Figure 1. Recent improvements of nuclear instrumentation and techniques allowed accurate measurements of natural radioactive isotopes and it is now believed that radioactive equilibrium between the long-lived isotopes of the uranium and thorium groups is more the exception than the rule in nature. Only a few years ago, it was assumed that the ^{234}U and ^{238}U isotopes were in equilibrium; however, it has been documented [1] that the ^{234}U content may vary between 60% deficient to 500% in excess relative to its parent, ^{238}U. An excess of 15% of ^{234}U isotope in sea water is well documented [2].

Pleistocene dating is one of the most useful applications of measurements of the extent of radioactive disequilibrium. Thorium and protactinium measurements in deep-sea sediment were used to date sediment horizons and to obtain rates of sedimentation which can be correlated with climatic changes and geological events [3]. Another application is dating of Pleistocene deposits by uranium, thorium, and protactinium analysis of coral and marine mollusk shells, therein [4,5].

The concentration levels of the isotopes under consideration are listed in Figure 1. Uranium content in common natural materials may vary from 0.1 to 50 parts per million (ppm). The data in Figure 1 are based on a

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[1] Publication authorized by the Director, U.S. Geological Survey.

NUCLIDE	WEIGHT (g)	ACTIVITY (D/MIN.)	NUCLIDE	WEIGHT (g)	ACTIVITY (D/MIN.)	NUCLIDE	WEIGHT (g)	ACTIVITY (D/MIN.)
^{238}U	1.00×10^{-6}	0.739	^{235}U	7.16×10^{-9}	0.0339	^{232}Th	3.50×10^{-6}	0.861
^{234}U	5.41×10^{-11}	0.739	^{231}Pa	3.21×10^{-13}	0.0339	^{228}Ra	1.41×10^{-15}	0.861
^{230}Th	1.61×10^{-11}	0.739	^{227}Ac	2.06×10^{-16}	0.0339	^{228}Th	4.72×10^{-16}	0.861
^{226}Ra	3.41×10^{-13}	0.739	^{227}Th	4.82×10^{-19}	0.0339	^{224}Ra	2.42×10^{-18}	0.861

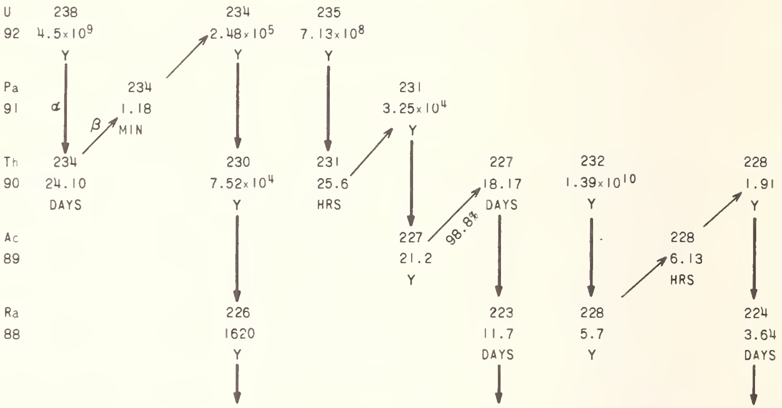

Figure 1. Uranium and thorium decay series and concentration of isotopes in series in equilibrium with parents.

uranium content of 1 (ppm) and the daughter elements are defined to be in equilibrium with the parents. The values in the ^{232}Th series are based on an average $^{232}Th/^{238}U$ ratio of 3.5 by weight. The total amount of ^{231}Pa in samples irradiated was commonly about 10^{-11} to 10^{-12} gram.

Uranium-238 and ^{232}Th were determined by mass spectrometry using the technique of isotope dilution [6]. The $^{234}U/^{238}U$ ratio was measured by alpha and/or mass spectrometry, and the $^{230}Th/^{232}Th$ ratio was measured by alpha spectrometry. Protactinium has been measured directly by alpha counting [4] and daughter products, ^{227}Th and ^{223}Ra, have been measured [7] to determine protactinium content. However, a direct ratio determination of $^{231}Pa/^{235}U$ is more accurate for these studies; therefore, we developed an activation technique for protactinium analysis in which ^{231}Pa is transformed partially to ^{232}U.

II. Experimental

The nuclear reactions associated with this technique are shown in Figure 2. The transformation of ^{232}Th to ^{233}U by thermal neutrons provides us with a very good intrinsic flux monitor when the $^{238}U/^{232}Th$ ratio in the sample is determined by the technique of isotope dilution.

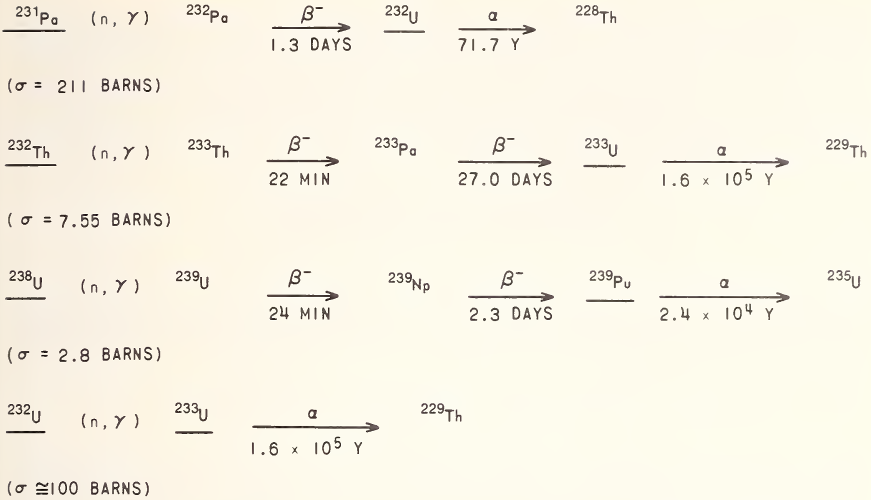
231Pa (n, γ) 232Pa β⁻ 1.3 DAYS 232U α 71.7 Y 228Th
(σ = 211 BARNS)
232Th (n, γ) 233Th β⁻ 22 MIN 233Pa β⁻ 27.0 DAYS 233U α 1.6 × 10⁵ Y 229Th
(σ = 7.55 BARNS)
238U (n, γ) 239U β⁻ 24 MIN 239Np β⁻ 2.3 DAYS 239Pu α 2.4 × 10⁴ Y 235U
(σ = 2.8 BARNS)
232U (n, γ) 233U α 1.6 × 10⁵ Y 229Th
(σ ≅100 BARNS)

Figure 2. Principal nuclear reactions involved in activation analysis of ^{231}Pa.

A. IRRADIATION

A thermal neutron irradiation of 2.5×10^{19} neutrons/cm^2 (nvt) appears to be about the optimum amount yielding a ^{232}U/^{238}U activity ratio of 0.1. This amount was obtained by irradiation for 40 hours at a thermal neutron flux of approximately 1.7×10^{14} n·cm^{-2}·sec^{-1}. The MTR facilities at the National Reactor Testing Station, Idaho, were used for irradiating samples. Samples weighing from 1 gram to 20 grams depending or uranium content were encapsulated in type 1100 aluminum capsules. References that are in radioactive equilibrium were irradiated along with samples for which the ^{231}Pa/^{235}U ratio was to be determined.

B. SEPARATIONS AND MEASUREMENTS

Analytical techniques for the separation of uranium have been described in detail [6] and only a slightly modified procedure was used for irradiated samples. Following sample decomposition with mixed acids, uranium was purified by anion exchange and hexone extraction. The interfering ^{239}Pu and ^{210}Po isotopes were separated from uranium by anion exchange. To ensure complete removal of polonium from uranium, a ^{208}Po spike was added prior to sample decomposition.

Measurements on electrodeposited uranium were made using silicon surface barrier detectors, solid state preamplifiers, amplifiers, and biased amplifiers. Up to four samples are measured simultaneously with a 400 channel analyzer. An alpha spectrum of uranium isotopes after chemical separation is shown in Figure 3. The sample from which this spectrum was obtained contained no measurable ^{232}Th, so the ^{233}U peak is absent; otherwise, the ^{233}U spectrum would overlap the ^{234}U spectrum. By integration of counts under the peaks, the ^{238}U/^{232}U and (^{233}U + ^{234}U)/^{238}U ratios are measured directly.

III. Results and Discussion

A. RESULTS

The following equations are useful to demonstrate the precision of the ^{231}Pa/^{235}U measurement.

$$^{233}\mathrm{U}/^{238}\mathrm{U} = (^{233}\mathrm{U} + {}^{234}\mathrm{U})/^{238}\mathrm{U} - {}^{234}\mathrm{U}/^{238}\mathrm{U} \qquad (1)$$

where ^{234}U/^{238}U was determined by mass-spectrometric measurement [6] or alpha-spectrometric measurement on non-irradiated portion of the sample.

$$^{233}\mathrm{U}\ \text{flux factor (f.f.)} = \frac{^{238}\mathrm{U\ (ppm)}}{^{232}\mathrm{Th\ (ppm)}} \frac{1}{[1-e^{-\lambda t}]} \frac{^{233}\mathrm{U}}{^{238}\mathrm{U}} \qquad (2)$$

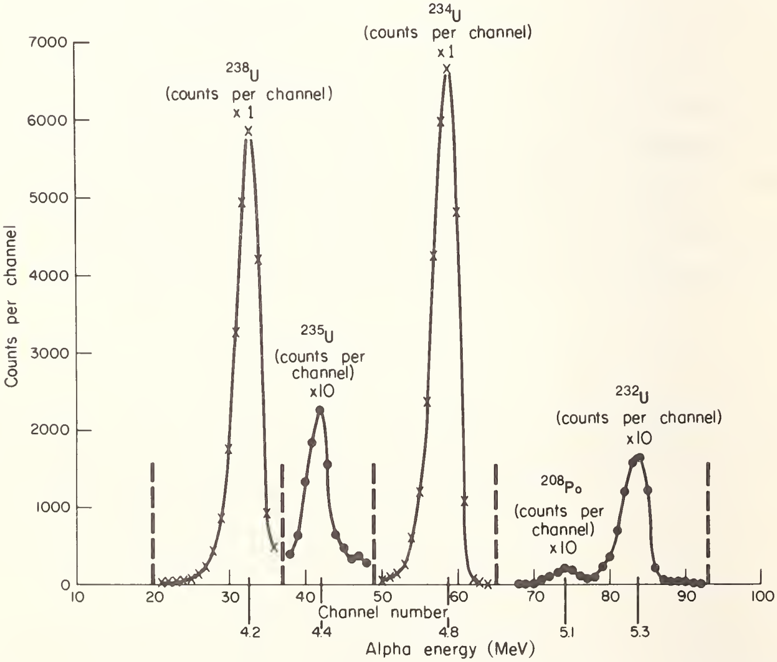

Figure 3. Alpha-energy spectrum of uranium isotopes separated from sample irradiated with 6×10^{18} nvt.

where $\frac{^{238}\text{U (ppm)}}{^{232}\text{Th (ppm)}}$ was determined by the technique of isotope dilution [6], λ is the decay constant of ^{233}Pa, and t is the interval elapsed between the median time of irradiation of the sample and the time of separation of protactinium from uranium.

$$\frac{^{231}\text{Pa}}{^{235}\text{U}} = \frac{[(\text{f.f.})^{238}\text{U}/^{232}\text{U}]\text{ reference}}{[(\text{f.f.})^{238}\text{U}/^{232}\text{U}]\text{ sample}} \tag{3}$$

For samples that contain very little ^{232}Th, it is possible to use the difference between the large fission-cross section of ^{235}U and the smaller capture-cross section of ^{238}U for an intrinsic flux monitor:

$$^{235}\text{U flux factor} = {}^{238}\text{U}/^{235}\text{U (irr.)} - {}^{238}\text{U}/^{235}\text{U (Nat.)} \tag{4}$$

where ^{238}U/^{235}U (irr.) is the atomic ratio in irradiated uranium and ^{238}U/^{235}U (nat.) is the natural atomic ratio in unirradiated uranium, both measured by high precision mass spectrometry.

Several irradiations and measurements were made on the granite reference sample (#3633), which contained 24 (ppm) uranium and 83 (ppm) thorium with ^{231}Pa in radioactive equilibrium with ^{235}U [8]. Measured activity ratios, flux factors (f.f.), and ^{238}U/^{232}U ratios normalized for flux factors are listed in Table 1. Values in column (f.f.) indicate the magnitude of variation of total thermal neutron flux available to the whole sample; variations greater than ±10% can occur during longer irradiation times. The relatively small variations of the normalized

Table 1. Activity ratios and flux factors in irradiated granite reference.

3633 reference No.	Length of irradiation (hours)	$\frac{^{238}U}{^{232}U}$	(f.f.)	(f.f.) $\times \frac{^{238}U}{^{232}U}$
1	1.5	203	0.232	47.1
2	1.5	206	0.231	47.6
3	10.0	41.8	1.29	52.9
4	10.0	39.1	1.20	47.0
5	10.0	37.3	1.37	51.1
6	40.0	9.94	4.82	47.9
7	40.0	8.23	5.96	49.0
8	40.0	9.85	4.83	47.5
9	40.0	10.5	4.48	47.0
		Average and standard deviation		48.6 ± 2.0

^{238}U/^{232}U ratios, after longer irradiation times, demonstrate the advantage of an intrinsic flux monitor for increasing the precision of measurements.

Another application of protactinium analysis is in the study of fractionation of elements in magmatic processes. The ^{231}Pa/^{235}U activity ratios in several volcanic rocks are listed in Table 2. Where analyses have been completed, ^{230}Th/^{234}U and ^{234}U/^{238}U ratios also are listed. The characteristic pattern for Holocene volcanic rocks (less than 10,000 years since eruption) is excess ^{231}Pa and excess ^{230}Th compared to ^{235}U and ^{234}U parents. Possible causes of the fractionation between elements are not yet apparent; however, some interpretations for Hawaiian basalt have been described [9].

B. Discussion

The presence of an intrinsic flux monitor built in the sample such as ^{232}Th is of great advantage for accurate determination of ^{231}Pa by activation analysis. Another intrinsic flux monitor, uranium, may be especially useful for samples that do not contain sufficient ^{232}Th. The atomic ratio of ^{238}U/^{235}U is changed from the normal value of 137.8 to 140.2 after irradiation with 2.5×10^{19} (nvt), as measured by precision

Table 2. Activity ratios of ^{234}U/^{238}U, ^{230}Th/^{234}U, and ^{231}Pa/^{235}U and uranium and thorium concentration in volcanic rocks.

	Activity ratio				
Sample description	^{234}U/^{238}U	^{230}Th/^{234}U	^{231}Pa/^{235}U	Uranium (ppm)	Thorium (ppm)
Basalt, Hawaii, 1801 flow	1.00 ± .01	1.27 ± .04	1.74 ± .06	0.54	1.90
Pumice, Iceland, Holocene	1.00 ± .01		1.11 ± .04	1.42	4.40
Pumice, Iceland, Holocene	1.00 ± .01		1.15 ± .04	1.55	4.81
Pumice, Iceland, Holocene	1.00 ± .01	1.20 ± .05	1.34 ± .05	2.07	7.45
Pumice, Iceland, Holocene	1.00 ± .01	1.08 ± .04	1.20 ± .04	2.24	7.22
Pumice, Iceland, Holocene	1.00 ± .01	1.46 ± .04	1.17 ± .04	2.62	11.32
Obsidian, Medicine Lake, California, Holocene			1.08 ± .01	5.19	13.8
Obsidian, Medicine Lake, California, Holocene	1.00 ± .01	1.09 ± .03	1.54 ± .05	5.68	15.3
Obsidian, Salton Sea, California, Holocene			1.07 ± .04	6.06	19.5
Obsidian, Salton Sea, California, Holocene			1.08 ± .04	6.08	20.8
Obsidian, Yellowstone, Wyoming, Late Pleistocene			1.12 ± .04	5.97	34.4
Obsidian, Nevada ~ 7 million years old	1.00 ± .01	1.04 ± .03	1.01 ± .05	5.31	23.5
Obsidian, Nevada ~ 7 million years old	1.01 ± .01	1.03 ± .03	1.01 ± .05	15.3	35.7
Obsidian, Nevada ~ 7 million years old	1.01 ± .01	1.04 ± .03	1.06 ± .05	45.9	223

solid-source mass spectrometry. Increasing the irradiation to more than 5 × 10^{19} nvt apparently would be desirable if this flux monitor is used in order to increase the difference between atomic ratios of $^{238}U/^{235}U$ for irradiated uranium and natural uranium.

IV. References

[1] Dooley, J. R., Jr., Granger, H. C., and Rosholt, J. N., Econ. Geol. **61,** 1362 (1966).
[2] Rona, Elizabeth, Science **144,** 1595 (1964).
[3] Rosholt, J. N., Emiliani, C., Geiss, J., Koczy, F. F., and Wangersky, P. J., Jour. Geology **69,** 162 (1961).
[4] Ku, Teh-Lung, Jour. Geophys. Res. **73,** 2271 (1968).
[5] Rosholt, J. N., Symposium on Radioactive Dating and Methods of Low-Level Counting, IAEA, Monaco, 299 (1967).
[6] Rosholt, J. N., Doe, B. R., and Tatsumoto, M., Geol. Soc. Amer. Bull. **77,** 987 (1966).
[7] Rosholt, J. N., Anal. Chem. **29,** 1398 (1957).
[8] Rosholt, J. N., Peterman, Z. E., and Bartel, A. J., U.S. Geol. Survey Prof. Paper 575-B, B133 (1967).
[9] Somayajulu, B. L. K., Tatsumoto, M., Rosholt, J. N., and Knight, R. J., Earth and Planet. Sci. Letters **1,** 387 (1966).

USE OF A Ge(Li) DETECTOR AFTER SIMPLE CHEMICAL GROUP SEPARATION IN THE ACTIVATION ANALYSIS OF ROCK SAMPLES.

IV. SIMULTANEOUS DETERMINATION OF STRONTIUM AND BARIUM

H. Higuchi and K. Tomura

The Institute for Atomic Energy
Rikkyo University
Yokosuka, Japan

H. Takahashi, N. Onuma, and H. Hamaguchi

Department of Chemistry
Faculty of Science
The University of Tokyo
Hongo, Tokyo, Japan

I. Introduction

One of the important advances in nuclear counting technique in recent years is the development of lithium drifted germanium [Ge(Li)] gamma-ray detector. The principal advantage of Ge(Li) detectors over the NaI(Tl) scintillation detector is much better resolution of the former. Several authors have made good use of Ge(Li) detectors in instrumental neutron activation analysis (INAA) of geochemical samples. Schroeder *et al* [1,2] demonstrated applications of Ge(Li) detectors in a wide variety of activation analysis studies. Cobb [3] showed that abundances of Mn, Sc, Th and several rare earth elements in various types of rocks can be determined by INAA using Ge(Li) gamma-ray spectrometry. Recently, Gordon *et al* [4], reported on the INAA of as many as 28 elements in various rocks.

Although Ge(Li) detectors have a much higher resolution than the conventional NaI(Tl) scintillators, the photopeak efficiency of the former detectors is much lower than that of the latter. For this reason, when the measurement is to be made in the low gamma-ray energy range, background in this region introduces serious problems in attaining good sensitivity for the INAA with Ge(Li) detectors. The high background level is largely due to Compton plateaus from higher energy gamma rays.

To improve the poor sensitivity of Ge(Li) detectors in applications to neutron activation analysis of geochemical and cosmochemical samples, our group employed simple chemical group separations before gamma counting in order to diminish the background and eliminate spectral interferences. Thus, an adequate combination of the Ge(Li) detector and chemical group separation has been successfully applied to the determination of rare earth elements [5,6], rubidium and cesium [7] in rock samples by neutron activation analysis.

The present paper reports the rapid simultaneous determination of strontium and barium in a number of standard rock samples using a Ge(Li) detector after short sample irradiation and rapid chemical group separation by a conventional precipitation method [8].

II. Experimental

A. Samples and Irradiations

Samples of six U.S.G.S. standard rocks were studied. Samples (500 mg each) were sealed in polyethylene ampoules. A 10 μl aliquot each of the reference standard solution of Sr and Ba (23 mg Sr/ml, 15 mg Ba/ml) was impregnated into a piece of filter paper and sealed in a polyethylene ampoule. Samples and the reference standards were irradiated for one hour at a neutron flux of *ca.* $1.5 \times 10^{12} \mathrm{n \cdot cm^{-2} \cdot sec^{-1}}$, using the TRIGA MARK-II reactor of Rikkyo University.

B. Procedure

The irradiated sample was decomposed by sodium peroxide fusion in a nickel crucible containing Sr and Ba carriers. The melt was dissolved with water and minimum amounts of conc. HCl. After putting in a hydroxide scavenge by adding conc. NH_4OH solution, the Sr and Ba carbonate mixture was precipitated by adding 10% Na_2CO_3 solution to the supernatant solution. The precipitate was dissolved in 10 ml of fuming HNO_3 and cooled in ice to precipitate Sr and Ba nitrates. The nitrate mixture was dissolved in 10 ml of water and 2 ml of conc. NH_4OH solution, and the Sr and Ba carbonate mixture was again precipitated. After washing twice with water, the carbonate mixture was spun down to the bottom of 1 cm diameter polyethylene tube and transferred to a Ge(Li) detector for gamma counting. The irradiated reference standard was dissolved in a small amounts of conc. HCl in the presence of the Sr and Ba carriers, and treated with the same chemical procedure stated above (except the hydroxide scavenge and nitrate precipitation step) so as to obtain the same counting geometry as the samples. Time required for the chemical separation was 1.5 h for 5 samples.

C. COUNTING

The active volume of the Ge(Li) detector used was estimated to be approximately 9.6 ml. The detector was operated in a vacuum at 77 °K with a bias voltage of 1080 V. The output signal from the detector was fed into an ORTEC Model 118A preamplifier and an ORTEC Model 410 linear amplifier. The resultant pulse was then analyzed by an RCL 400 channel pulse-height analyzer. Resolution for the ^{57}Co 122-keV peak was 3 keV. The 388-keV photopeak of ^{87m}Sr (2.83 h) and 166-keV photopeak of ^{139}Ba (82.9 min.) were used for the determination of Sr and Ba, respectively.

D. CHEMICAL YIELD DETERMINATION

The chemical yields of Sr and Ba were obtained by a simple reactivation technique without any additional chemical treatment.

III. Results and Discussion

Strontium and barium abundances found in the six geochemical standard rocks are summarized in Table 1. In Table 2, the mean values for these standard rocks are compared with the recommended values given by Fleischer [9], and with reported values of Flanagan [10], Schnetzler *et al* [11], Nicholls *et al* [12] and Gordon *et al* [4]. It is shown in Table 1 that the values of duplicate analyses agree well within the experimental errors. As shown in Table 2, the close agreement with previously reported values for all of these geochemical standard rocks also indicates that the accuracy for the present procedure is good.

Table 1. Concentrations of strontium and barium in several geochemical standard rocks.

Sample	Split/Position	Strontium (ppm)	Barium (ppm)
G−1		256 ± 4	1005 ± 20
(Granite)		254 ± 11	1050 ± 33
	Average	256 ± 4	1015 ± 17
W−1		192 ± 3	161 ± 3
(Diabase)		195 ± 6	178 ± 4
	Average	193 ± 3	167 ± 3
G−2	54/10	442 ± 14	1640 ± 40
(Granite)		446 ± 14	1610 ± 41
	Average	445 ± 10	1627 ± 29

Table 1. Concentrations of strontium and barium in several geochemical standard rocks (continued).

Sample	Split/Position		Strontium (ppm)	Barium (ppm)
GSP – 1	13/22		220 ± 7	1102 ± 22
(Granodiorite)			242 ± 14	1168 ± 20
		Average	224 ± 7	1137 ± 15
AGV – 1	26/3		617 ± 22	1040 ± 22
(Andesite)			597 ± 38	1128 ± 44
		Average	612 ± 19	1060 ± 20
BCR – 1	39/20		332 ± 15	623 ± 16
(Basalt)			325 ± 10	626 ± 13
		Average	327 ± 9	625 ± 10

Note: The errors in the third and fourth columns were calculated from the counting statistics. The averages have been computed by suitable weighting.

Table 2. Comparison of strontium and barium concentrations in several geochemical standard rocks.

Sample	Strontium (ppm)	Barium (ppm)	Method	Reference	
G–1	250	1220	Recommended Value	Fleischer	(1965)
	– – –	1039	Isotope Dilution	Schnetzler et al.	(1966)
	256 ± 4	1015 ± 17	Neutron Activation	This Work	
W–1	180	180	Recommended Value	Fleischer	(1965)
	– – –	158	Isotope Dilution	Schnetzler et al.	(1966)
	175	145	Spark Source Mass Spectrography	Nicholls et al.	(1967)
	– – –	<200	Neutron Activation	Gordon et al.	(1968)
	193 ± 3	167 ± 3	Neutron Activation	This Work	
G–2	340–500	1400–2000	Emission Spectrography	Flanagan	(1967)
	– – –	1800 ± 70	Neutron Activation	Gordon et al.	(1968)
	445 ± 10	1627 ± 29	Neutron Activation	This Work	
GSP–1	220–300	1000–1600	Emission Spectrography	Flanagan	(1967)
	– – –	1110 ± 50	Neutron Activation	Gordon et al.	(1968)
	224 ± 7	1137 ± 15	Neutron Activation	This Work	
AGV–1	610–900	1200–1800	Emission Spectrography	Flanagan	(1967)
	– – –	1180 ± 100	Neutron Activation	Gordon et al.	(1968)
	612 ± 19	1060 ± 20	Neutron Activation	This Work	
BCR–1	300–410	460–880	Emission Spectrography	Flanagan	(1967)
	– – –	650 ± 30	Neutron Activation	Gordon et al.	(1968)
	327 ± 9	625 ± 10	Neutron Activation	This Work	

In the INAA with a Ge(Li) detector reported by Gordon *et al* [4], it was difficult to determine Ba in W-1 and the detection limit was 200 parts per million (ppm) Ba for W-1. Sr in various rocks could not be determined by the INAA. While the present procedure is attainable to the lower detection limit (Sr 10 ppm, Ba 5 ppm), the technique is applicable for the determination of both elements in geochemically imporant rock samples.

IV. References

[1] Schroeder, G. L., Kraner, H. W., and Evans, R. D., Science **151,** 815 (1966).

[2] Schroeder, G. L., Evans, R. D., and Ragaini, R. C., Anal. Chem. **38,** 432 (1966).

[3] Cobb, J. C., Anal. Chem. **39,** 127 (1967).

[4] Gordon, G. E., Randle, K., Goles, G. G., Corliss, J. B., Beeson, M. H., and Oxley, S. S., Geochim. Cosmochim. Acta **32,** 369 (1968).

[5] Tomura, K., Higuchi, H., Miyaji, N., Onuma, N., and Hamaguchi, H., Anal. Chim. Acta **41,** 217 (1968).

[6] Tomura, K., Higuchi, H., Onuma, N., and Hamaguchi, H., Anal. Chim. Acta, in press.

[7] Tomura, K., Higuchi, H., Takahashi, H., Onuma, N., and Hamaguchi, H., Anal. Chim. Acta, in press.

[8] Higuchi, H., Tomura, K., Takahashi, H., Onuma, N., and Hamaguchi, H., submitted for publication in Anal. Chim. Acta (August, 1968).

[9] Fleischer, M., Geochim. Cosmochim. Acta **29,** 1263 (1965).

[10] Flanagan, F. J., Geochim. Cosmochim. Acta **31,** 289 (1967).

[11] Schnetzler, C. C., Thomas, H. H., and Philpotts, J. A. Geochim. Cosmochim. Acta **31,** 95 (1967).

[12] Nicholls, G. D., Graham, A. L., Williams, E., and Wood, M., Anal. Chem. **39,** 584 (1967).

ACTIVATION ANALYSIS OF GEOCHEMICAL MATERIALS USING Ge(Li) DETECTORS

Royston H. Filby and William A. Haller

Nuclear Reactor
Washington State University
Pullman, Washington 99163

I. Introduction

The advantages of neutron activation analysis applied to geochemical problems are well known. Instrumental neutron activation analysis for many elements is now possible through use of high resolution Ge(Li) detectors and several recent publications [1-3] describe its application to geochemical samples. Except for Na, Mn, and K, only elements of relatively long half lives have been measured by this technique.

The work described in this paper was undertaken to extend the range of elements which may be determined in rocks, minerals and meteorites. To include nuclides with half lives in the range 2 minutes to 40 hours, the method developed consists of three parts. Short neutron irradiation of samples and standards followed by rapid transfer to the counting system permits the determination of Al, Mn, Na, V, Ti, Ca, and in certain cases, Mg, in rocks and meteorites. Long irradiation followed by a one month decay period allows the determination of Sb, Co, Zn, Sc, Cr, Eu, Th, U, Ba, Ta, and Fe. The high ^{24}Na activity in most irradiated silicate rocks and meteorites masks several (n,γ) activation products of interest, for example, ^{42}K, ^{72}Ga, ^{69m}Zn, ^{140}La, ^{64}Cu, ^{87m}Sr, ^{139}Ba, ^{152m}Eu, and in certain cases, ^{56}Mn (low manganese). A method has been developed for the determination of these nuclides by the dissolution of the irradiated sample followed by removal of ^{24}Na on a sodium specific inorganic ion-exchanger. The separation of ^{24}Na is simple and negligible adsorption of other elements of interest has been observed.

II. Experimental

A. Apparatus and Reagents

20 cm^3 Ge(Li) detector (Nuclear Diodes) 3.2 keV resolution full width half maximum (FWHM) 1.33 MeV ^{60}Co); Canberra 1408 preamplifier; Canberra 1416 amplifier.

Nuclear Data ND2200 4096 channel analyzer with magnetic tape/fast print readout modes.

Sodium ion exchanger; RA-1 ERBA; Carlo Erba, Milan, Italy. Lithium metaborate; double quartz distilled nitric acid and water.
Carrier solution; Ga, La, K, Mn, Zn, Cu, Eu, Sr, and Ba mg per ml of each element in 8 *M* nitric acid.

B. Procedure

Rock and meteorite samples were sealed in polyethylene irradiation capsules. The capsules had been leached to remove impurities with double-distilled nitric acid followed by double distilled water. The analytical method was performed in three stages, and the nuclear reactions and gamma-ray energies used are shown in Table 1.

1. Determination of Al, Ca, Na, Mn, Ti, V, and Mg

Samples and appropriate standards were irradiated in the "rabbit" facility of the Washington State University TRIGA III-type reactor in a

Table 1. Nuclear reactions and gamma-ray energies [6].

Element	(n, γ) product	Half life	Gamma ray used (MeV)
Aluminum	^{28}Al	2.31 min	1.78
Magnesium	^{27}Mg	9.5 min	1.01
Calcium	^{49}Ca	8.8 min	3.10
Sodium	^{24}Na	15.0 h	1.37
Manganese	^{56}Mn	2.58 h	0.845
Titanium	^{51}Ti	5.8 min	0.323
Vanadium	^{52}V	3.76 min	1.43
Copper	^{64}Cu	12.8 h	0.511
Zinc	^{69m}Zn	13.8 h	0.440
Gallium	^{72}Ga	14.1 h	0.835
Lanthanum	^{140}La	40.2 h	1.60
Europium	^{152m}Eu	9.3 h	0.963
Chromium	^{51}Cr	27.8 d	0.320
Scandium	^{46}Sc	83.9 d	0.889
Cobalt	^{60}Co	5.26 y	1.173
Barium	^{131}Ba	12.0 d	0.374
Antimony	^{124}Sb	60 d	1.70
Tantalum	^{182}Ta	115 d	1.189

thermal neutron flux 5 × 10^{12}n·cm^{-2}·sec^{-1} for 30 seconds to two minutes. Samples were transferred pneumatically to the Ge(Li) spectrometry system and counted at regular intervals to establish the decay of ^{28}Al, ^{49}Ca, ^{51}Ti, ^{52}V, ^{24}Na, ^{56}Mn and ^{27}Mg. Figure 1 shows a spectrum of W-1 four minutes after irradiation.

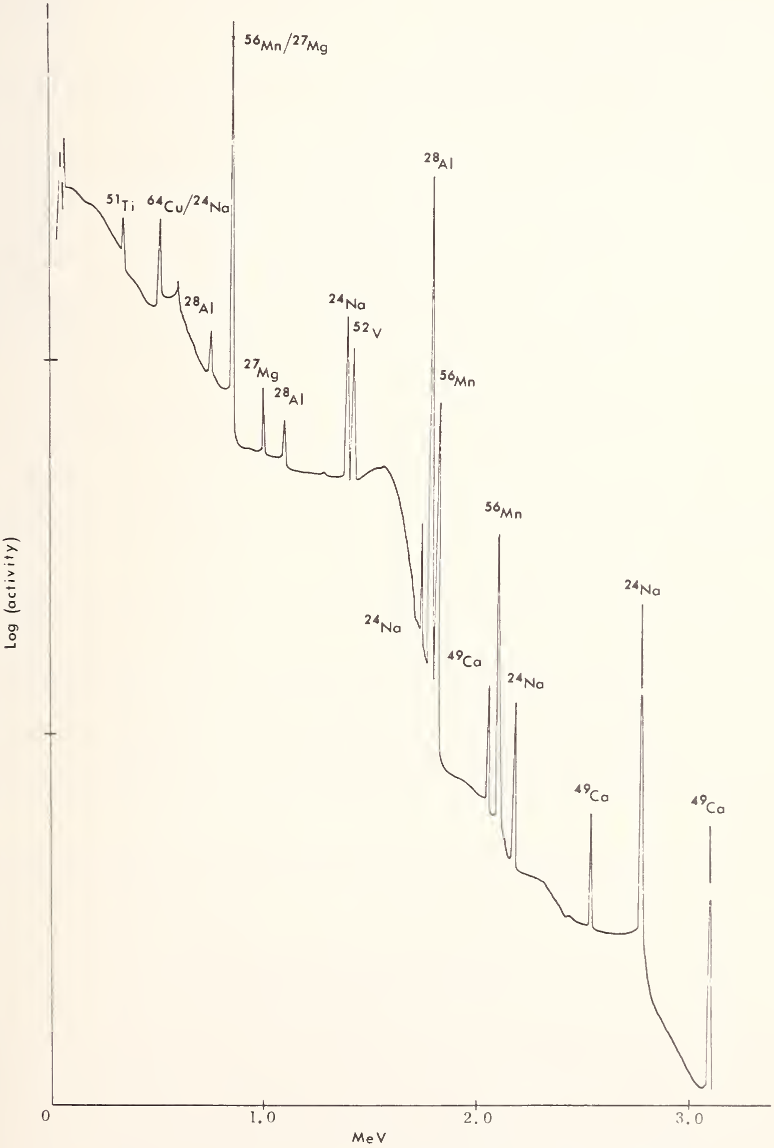

Figure 1. 20 cm^3 Ge(Li) spectrum of W-1, 4 minutes after irradiation.

2. *Determination of K, Mn, Ga, Eu, Zn, La, Cu, Sr, and Ba*

Samples (0.3-1.0 g) were irradiated for one to two hours in a thermal neutron flux of $8 \times 10^{12} n \cdot cm^{-2} \cdot sec^{-1}$. After "cooling" for one hour to allow short-lived activities (principally ^{28}Al) to decay, the samples were decomposed by one of two methods.

a. For Silicates and the Silicate Phases of Meteorites. Fusion with $LiBO_2$ at 800 °C for 5 minutes was carried out. The melts were then dissolved in 8 *M* nitric acid.

b. For Limestones, Dolomites and the Iron Phase of Meteorites. The samples were dissolved in 6 *M* hydrochloric acid and an equal volume of 10 *M* nitric acid was added.

To the solution of the rock, 5 ml of carrier solution were added followed by 1 g of RA-1 ion exchanger. The solution was shaken for 30 minutes centrifuged and the RA-1 washed twice with 8 *M* nitric acid. The process was repeated and the solution counted immediately for ^{56}Mn, ^{87m}Sr and ^{139}Ba. Twelve hours later the solution was recounted to determine ^{42}K, ^{64}Cu, ^{152m}Eu, ^{69m}Zn, ^{72}Ga, and ^{140}La. ^{24}Na distribution ratios, *D*, were calculated from the equation:

$$D = \frac{^{24}\text{Na activity counts per minute (cpm) in RA}-1}{^{24}\text{Na activity of solution}} \tag{1}$$

Figure 2 shows a spectrum of W-1 after separation of ^{24}Na by the process described.

3. *Determination of Fe, Sc, Co, Sb, Zn, Eu, Th, U, Ba, Ta, Hf, Cr*

Samples (0.5 to 1.5 g) and standard solutions were irradiated for 8 hours in a thermal neutron flux of $8 \times 10^{12} n \cdot cm^{-2} \cdot sec^{-1}$. To ensure flux uniformity samples and standards were rotated about a vertical axis in the reactor core. Samples were allowed to decay for 3 to 4 weeks and then counted for at least 1000 minutes. Samples were then recounted after two months.

In all methods conventional techniques were used to calculate gamma-ray peak areas and to process the data.

III. Results and Discussion

Results for some major and trace elements in seven standard rocks are shown in Tables 2 and 3. Table 2 shows results obtained for major elements and Table 3 lists results for trace elements. Data will also be presented for 10 chondrites and 3 achondrites and 3 carbonate rocks. The standard deviations shown in Tables 2 and 3 were calculated from

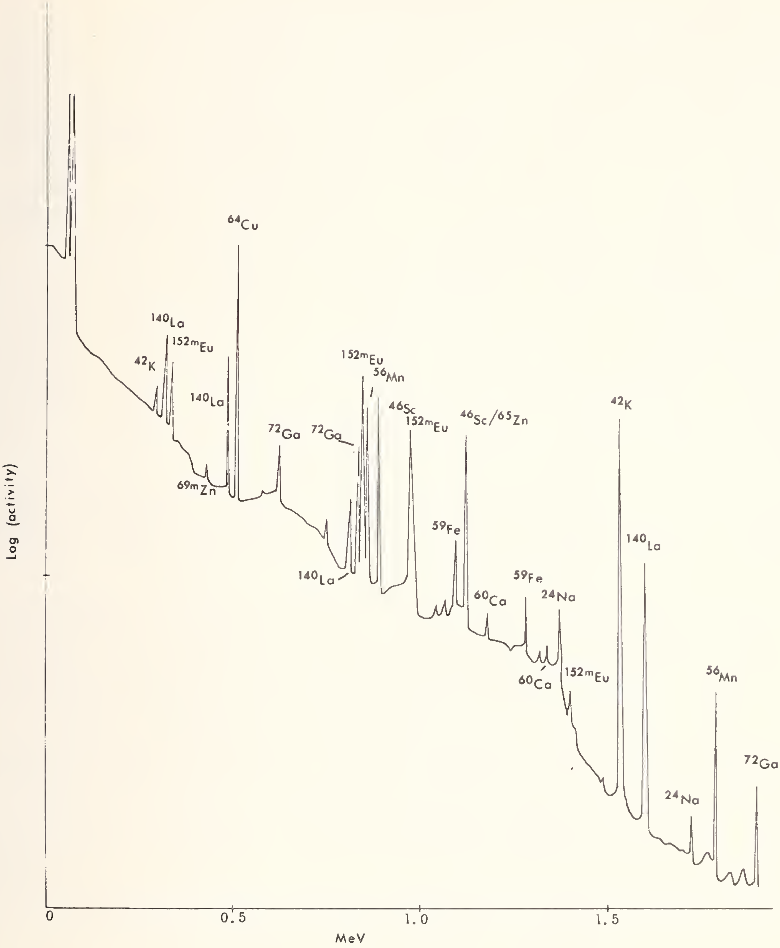

Figure 2. Ge(Li) spectrum of W-1 after ^{24}Na separation.

counting statistics. Where feasible at least 5000 counts were accumulated under the peak of interest.

Also shown in Tables 2 and 3 are data obtained by other workers [3-5]. In general, good agreement is found between the major element data presented here and those obtained previously with the exception of potassium. The potassium results obtained are however in reasonably good agreement with the instrumental neutron activation analysis values of Gordon *et al* [3]. The trace element data also agree well with those of Gordon *et al* [3] with the exception of La. No reason has been found so far for the low results obtained in this study.

Table 2. Major elements in silicates (%).

Elements	W – 1	AGV – 1	BCR – 1	G – 2	GSP – 1	PCC – 1	DTS – 1
Aluminum							
This work	7.67±.2	9.2 ±.15	7.7 ±.3	8.0 ±.2	8.5 ±.15	.39 ±.05	.16 ±.01
Other [4,5]	7.94	9.05	7.25	8.16	8.12	.41	.16
Magnesium							
This work	– – –	– – –	– – –	– – –	– – –	25.7 ±.8	28.3 ±.9
Other [4,5]	– – –	– – –	– – –	– – –	– – –	26.15	30.07
Calcium							
This work	7.92±.12	3.39±.15	4.99±.15	1.30 ±.2	1.2 ±.3	– – –	– – –
Other [4,5]	7.82	3.49	4.94	1.42	1.48	– – –	– – –
Iron							
This work	7.60±.15	– – –	– – –	1.65 ±.2	– – –	– – –	– – –
Other [4,5]	7.76	– – –	– – –	1.85	– – –	– – –	– – –
Sodium							
This work	1.61±.02	3.08±.02	2.11±.04	3.016±.02	1.94±.05	0.022±.001	0.027±.001
Other [4,5]	1.53 – 1.68	2.99 – 3.15	2.33 – 2.46	2.89 – 3.07	1.90 – 2.10	.01	.04
Potassium							
This work	0.46±.01	2.25±.04	1.20±.02	– – –	3.95±.02	.012±.005	.018±.005
Other [4,5]	.53	2.37	1.42	– – –	4.56	n.d.	n.d.
[3]	.8	2.20	1.2	– – –	4.5		

Table 3. Trace elements in silicates (ppm).

Element	W – 1	AGV – 1	BCR – 1	G – 2	GSP – 1	DTS – 1	PCC – 1
Europium							
This work	1.0±.05	1.92±.1	2.23±.1	1.5± .2	2.48± .1	– – –	– – –
Other [3]	1.08	1.55	1.95	1.37	2.0	– – –	– – –
Lanthanum							
This work	6.7±.8	23.9 ±1	15.4 ±.9	– – –	105±.4	.05±.01	– – –
Other [3]	12	33	23	– – –	170	– – –	– – –
Scandium							
This work	33±1	12±1	36±1	4.0± .2	– – –	1.0	1.–
Other [3]	34	12	33	3.5	– – –	– – –	– – –
Vanadium							
This Work	304±20	160±30	340±30	– – –	– – –	– – –	– – –
Other [4]	240	80 – 150	170 – 500	– – –	– – –	– – –	– – –
Tantalum							
This work	0.5±.15	1.7±.2	– – –	– – –	– – –	1.0 ±.1	– – –
Other [3]	0.67	1.0	– – –	– – –	– – –	– – –	– – –
Barium							
This work	– – –	1240±30	– – –	– – –	960±35	100	100
Other [3]	– – –	1180	– – –	– – –	1110	– – –	– – –
Antimony							
This work	0.8±.2	– – –	– – –	0.2±.1	3.0±.2	– – –	– – –
Manganese							
This work	1368±10	735±15	1365±10	248±5	– – –	904±15	921±20
Other [4,5]	1320	640	1300	212	– – –	840 – 1100	700 – 1200

Table 3. Trace elements in silicates (ppm). (continued)

Element	W – 1	AGV – 1	BCR – 1	G – 2	GSP – 1	DTS – 1	PCC – 1
Titanium							
This work	6900±200	6300±300	11,000	2600±300	– – –	n.d.	n.d.
Other [4,5]	6400	5000 – 7700	12000 – 13000	2200 – 2900	– – –	– – –	– – –
Copper							
This work	72.5±.9	49.0±.8	17.0±.6	– – –	28.8±1.0	5±0.5	14.0±.0
Other	110	55 – 100	19 – 39	– – –	34 – 60	3 – 9	7 – 15
Zinc							
This work	89±4	64±4	– – –	– – –	– – –	30±5	– – –
Other [4,5]	82	– – –	– – –	– – –	– – –	– – –	– – –
Chromium							
This work	95±5	10±1	– – –	7.2±1.9	– – –	3600±100	2400±100
Other [3]	99	8.6	– – –	4.6	– – –	2300 – 4600	1200 – 3600
Gallium							
This work	12.8±.3	16.6±.9	16.2±.8	– – –	16.4±.8	.89±.15	1.2±.3
Cobalt							
This work	50±2	17.0±.7	30±1	5.0±1	5.0±1	90±2	100±2
Other	46	14.7	36.3	4.3	7.0	– – –	– – –

^{24}Na distribution ratios were calculated from the analytical data in most instances. The distribution ratios obtained for four rocks and one meteorite are shown in Table 4. The excellent extraction of ^{24}Na is shown by the range of values of D (3.16×10^{-3} to 3.1×10^{-4}).

The extraction of Ga, Zn, K, La, Cu, Mn and Eu by the RA-1 exchanger were also studied by single batch equilibration experiments to ascertain that adsorption of these elements was negligible. The conditions of method (2) were reproduced and distribution ratios were calculated from

$$D = \frac{\text{concentration of element in solid phase}}{\text{concentration of element in solution}} \tag{2}$$

Table 4. ^{24}Na extraction results.

Rock	Normalized counts on resin[a]		Ratio	Ratio, D
	Resin 1	Resin 2	Resin 1/Resin 2	total/extract
AGV–1	236235	5934	40.37	4.94×10^3
GSP–1	146625	2463	59.53	
BCR–1	138419	4135	33.47	9.31×10^3
W–1	159478	3385	44.48	3.16×10^3
Bruderheim (chondrite)	–	–	–	7.0×10^3

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[a] All count rates are in counts/400 seconds.

Table 5 shows the results obtained and it is evident that the elements of interest other than sodium are not appreciably absorbed by the RA-1 exchanger.

Table 5. Extraction of potassium, gallium, zinc, manganese, europium, copper, and lanthanum by RA–1 ERBA.

Element	Concentration (mg/50 ml)	Distribution ratio D	Medium
Potassium	1.0	1.71×10^{-3}	$8\ M$ $HNO_3 - 0.01\ M$ Na^+
Gallium	1.0	4.70×10^{-4}	$8\ M$ $HNO_3 - 0.01\ M$ Na^+
Zinc	1.0	3.57×10^{-4}	$8\ M$ $HNO_3 - 0.01\ M$ Na^+
Manganese	1.2	3.12×10^{-4}	$6.5\ M$ HNO_3
Europium	1.0	2.1×10^{-4}	$8\ M$ $HNO_3 - 0.01\ M$ Na^+
Copper	1.0	3.6×10^{-4}	$8\ M$ $HNO_3 - 0.01\ M$ Na^+
Lanthanum	1.0	4.3×10^{-4}	$8\ M$ $HNO_3 - 0.01\ M$ Na^+

IV. References

[1] Cobb, J. C., Anal. Chem. **39,** 127 (1967).

[2] Prussin, S. G., Harris, J. A., and Hollander, J. M., Anal. Chem **37,** 1127 (1965).

[3] Gordon, G. E., Randle, K., Goles, G. G., Corliss, J. B., Beeson, M. H., and Oxley, S. S., Geochim. et Cosmochim. Acta **32,** 369 (1968).

[4] Flanagan, F. J., Geochim. et Cosmochim. Acta **31,** 289 (1967).

[5] Stevens, R. E., U.S. Geol. Survey Bull. 1116 (1960).

[6] Lederer, C. M., Hollander, J. M., and Perlman, I., Table of Isotopes, Wiley, New York 1967.

Ge(Li) DETECTORS IN THE ACTIVATION ANALYSIS OF GEOLOGICAL SAMPLES

Keith Randle and Gordon G. Goles

Center for Volcanology
University of Oregon
Eugene, Oregon

I. Introduction

NaI(Tl) detectors have been used for a number of years to study abundances of several elements in both terrestrial and meteorite samples. The method has been used most widely after extensive chemical separations of elements or groups of elements. Instrumental neutron activation analysis (INAA) *i.e.,* counting samples without any chemical separation, has been carried out with NaI(Tl) detectors, *e.g.* Schmitt, *et al,* [3]; Brunfelt and Steinnes, [2]; Stueber and Goles, [4]. However, because of the poor resolution of these detectors, comparatively few elements can be determined accurately this way from the complex spectra characteristic of rocks and meteorites.

The advent of Ge(Li) detectors with their much superior resolution has increased the number of elements that may be determined and in many cases markedly increased the accuracy of abundance measurement. The systems currently in use in our laboratory enable most of the geochemically important elements to be determined without recourse to any chemical separations. This both improves the time taken for the analysis of a rock and frequently increases the accuracy of determinations of trace elements.

II. Experimental Methods

Samples of approximately 1 gram in weight are normally required. These, together with 1 ml aliquots of monitor solutions of the desired elements, were irradiated in the rotating rack facility of a General Atomic TRIGA reactor. This enabled up to sixty samples and monitors for twenty-three elements to be irradiated at the same time. Two irradiations were normally made. The first was of ten minutes duration with a neutron flux of about 10^{11} n·cm^{-2}·sec^{-1}. This enabled manganese (^{56}Mn, half life 2.6 hours) and sodium (^{24}Na, half life 15.0 hours) to be determined and occasionally potassium (^{42}K, half life 12.4 hours). The second irradiation was for about six hours with the reactor at full power giving a flux of about 10^{12} n·cm^{-2}·sec^{-1}. The longer-lived species were generated at this time. Samples and monitors were in nearly identical radial and vertical positions with respect to the reactor core and the sample rack was rotated at 1 revolution/minute to insure a uniform neutron flux. After allowing for a suitable cooling time (several days in the case of the long irradiation) to allow unwanted activities to decay away the samples and monitors were transferred to clean two dram vials for counting.

Most of the data reported here were obtained using a 30 cm³ coaxial Ge(Li) detector (Nuclear Diodes). We are currently testing out a much larger detector which has an efficiency of 6.2% of that of a 3 in. × 3 in. NaI(Tl) well crystal. Signals from the detector were passed through a suitable pre-amplifier and linear amplifier and thence into either a 1024-channel analyzer (Nuclear Data) or a 4096-channel analyzer (Kicksort). These were calibrated such that spectra with lines from 0 to about 3 MeV in energy were studied. The detectors were shielded with a 4 inch lead shield to reduce the background. The background was fairly structureless, but some lines were observed (*e.g.* ^{40}K, 1462 keV). The counting vials were placed in milled depressions in a Lucite sample holder attached to the detector chamber.

A typical spectrum obtained with the 30 cm³ detector is shown in Figure 1. This spectrum was observed from a U.S.G.S. standard rock, the quartz monzonite GSP-1, about seven weeks after irradiation. As is generally the case for silicic rocks, the spectrum contains a great number

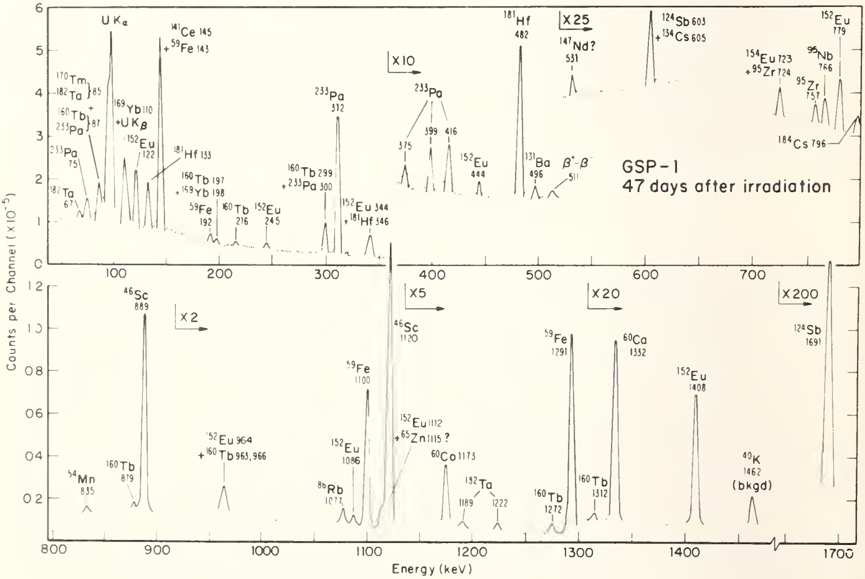

Figure 1. Spectrum of gamma-rays from GSP-1 observed with 30 cm³ Ge(Li) detector 47 days after neutron irradiation.

of lines, many of them from rare earths. More basic rocks tend to be dominated by lines from iron and scandium.

The resolution of the 30 cm³ detector was about 5.6 keV for the 1333 keV gamma rays of ^{60}Co. It was even better for the new high efficiency system being only 4.1 keV. The ratio of photopeak height to that of the Compton shoulder for 662 keV gamma rays was about 10 for the 30 cm³ detector and about 13 for the high efficiency one.

The spectrum in Figure 1 indicates the high density of lines up to about 150 keV, and this is true for both silicic and more basic rocks. In order to observe this region in more detail the samples and some of the monitors with low energy gamma rays were counted with a very high resolution system at the Lawrence Radiation Laboratory in Berkeley. This system employed a 1 cm² + 0.6 cm Ge(Li) detector having a thin dead-layer on the front surface; the window of the detector chamber consisted of a thin beryllium foil so that absorption of low energy gamma rays was kept to a minimum. This system had a very low counting efficiency but a resolution of 0.8 keV at about 100 keV (for further details see Bowman, *et al,* [1]. A typical spectrum observed with this system is shown in Figure 2. This was obtained with the U.S.G.S. standard basalt, BCR-1, some three months after irradiation. From these spectra, accurate determinations of neodymium (^{147}Nd), tantalum (^{182}Ta), and thulium (^{170}Tm) could be obtained which were otherwise impossible from spectra taken with the larger detectors.

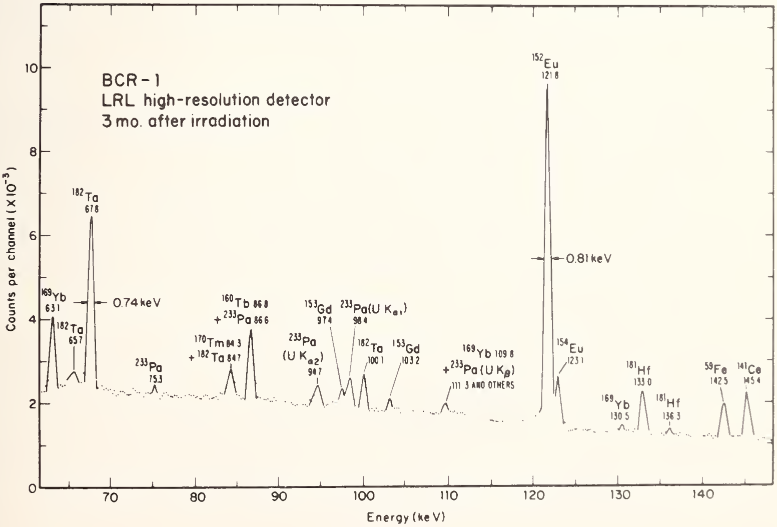

Figure 2. Low-energy portion of the gamma-ray spectrum emitted by BCR-1 about three months after neutron irradiation. Spectrum was taken with a very high resolution Ge(Li) detector at Lawrence Radiation Laboratory in Berkeley.

Identification of the observed gamma rays was based largely on the energies of the lines, which could easily be obtained to within ± 0.5 keV. The decay schemes of species produced by neutron activation in this work are all known with sufficient accuracy to identify the isotopes involved. Identification occasionally involved following the decay of a line and using known half lives to assign a species.

The system was calibrated with ^{109}Cd (88.2 keV), ^{137}Cs (661.6 KeV), ^{60}Co (1173 and 1333 keV) and ^{124}Sb (1691 keV). Using 1024 channels a calibration of 2 keV/channel was used and with the 4096 analyzer it was about 0.70 keV/channel. It was found that both systems were sufficiently stable so that they required calibrating only once in several weeks.

The data from the analyzers were read out on punched tape and this was then passed into a computer for reduction of the data. A calibration spectrum was first read in containing the spectrum from ^{109}Cd, ^{137}Cs, ^{60}Co and ^{124}Sb. The computer then calibrated the various portions of the spectrum from the known energies of these lines. This calibration could be checked against many lines of accurately known energy which appeared in every spectrum which thus acted as internal standards. The computer now determined the position (in channel numbers) and energy of every peak in the spectrum. From a predetermined set of criteria, the background (both real and that due to Comptons from high energy lines) in each portion of the spectrum was calculated and the areas of the peaks determined using a "window" of about 4 or 5 channels around the peak maximum. This area was then compared to the identical area in the monitor spectrum. From this ratio and applying corrections for decay between sample and monitor counts, different counting times, *etc.*, the abundance of the element could be obtained.

Each sample was observed at several different times after irradiation to optimize determinations for species of various half lives. Following the short irradiations, spectra of the samples were taken a few hours and about one day after the irradiation. After a long irradiation, samples were counted after five days, three weeks and several months. During each of the counting cycles, spectra of element monitors in the appropriate half-life range were taken under the same conditions.

Even with the high resolution of the Ge(Li) detectors, there are some multiple peaks that cannot be resolved into their components. In those cases it is often possible to remove contributions from species which have other gamma rays whose photopeak areas can be determined. Thus the computer must determine elements in a strict sequence. Results indicate that this can be successfully done in most cases. In some cases it was possible to base determinations of an element on more than one isotope (*e.g.* ^{169}Yb and ^{175}Yb).

In Table 1 we have listed the approximate lower limits of abundances which can be determined in silicic and in basic rocks. Sensitivities for elements having longer-lived products depend strongly upon the Co, Fe, and Sc contents of these rocks, and this is particularly severe for basic rocks.

The method has been used to try to distinguish between ash falls from several volcanic sites in Oregon. These act as important horizon markers in several areas. Since the eruptions are of known age, classification of the ashes is important for both geologists and archaeologists. Preliminary

Table 1. Production and properties of nuclides observable with Ge(Li) detectors.[a]

Element	Target isotope	Isotopic abundance (%)	Product nuclide	Effective $\sigma(n_{th},\gamma)$ (barns)	Best photopeak(s) used in determination (keV)	Best time after irradiation for counting	Sensitivity (ppm unless % indicated)	
							G−2	W−1
Na	^{23}Na	100	15.0-h ^{24}Na[b]	0.53	1369, 1732 (DE)	1 day	100	170
K	^{41}K	6.8	12.4-h ^{42}K	1.2	1524	1 day	0.7%	>2%
Rb	^{85}Rb	72.15	18.66-d ^{86}Rb	1	1077	2-4 wks.	40	>30
Cs	^{133}Cs	100	2.05-y ^{134}Cs	31	605, 796	few mo.	0.7	0.7
Ba	^{130}Ba	0.1	12-d ^{131}Cs	8.8	216, 373, 496	2-4 wks.	150	>200
La	^{139}La	99.9	40.22-h ^{140}La	8.9	329, 487, 816, 1596	4-5 days	5	2
Ce	^{140}Ce	88.5	33-d ^{141}Ce	0.6	145	2-4 wks.	12	4
Nd	^{146}Nd	17.1	11.1-d ^{147}Nd	2	91, 531	2-4 wks.	--	--
Sm	^{152}Sm	26.6	47-h ^{153}Sm	210	103	4-5 days	1	0.3
Eu	^{151}Eu	47.8	12-y ^{152}Eu	5,900	122, 245, 779, 1408	few mo.	0.1	0.3
			9.3-h $^{152^{m}1}$Eu	2,800	122, 842, 963	0.5-1 day	--	--
	^{153}Eu	52.2	16-y ^{154}Eu	320	724, 1277	few mo.	0.3	0.7
Gd	^{152}Gd	0.2	242-d ^{153}Gd	<180	97, 103	few mo.	--	--
Tb	^{159}Tb	100	72.1-d ^{160}Tb	46	299, 963+966	few mo.	0.1[c]	0.2[c]
Dy	^{164}Dy	28.2	2.32-h ^{165}Dy	2,700	95	few hrs.	--	--
Tm	^{169}Tm	100	130-d ^{170}Tm	125	84	few mo.	>0.4[c]	>0.3[c]
Yb	^{168}Yb	0.14	32-d ^{169}Yb	11,000	63, 177, 198	1 mo.	0.3	1.9
	^{174}Yb	31.8	4.21-d ^{175}Yb	55	283, 396	1-2 wks.	0.3	2.0
Lu	^{176}Lu	2.6	6.7-d ^{177}Lu	2, 100	208	2 wks.	0.1	0.09
Th	^{232}Th	100	22-m ^{233}Th$^{\beta}$	7.4				
			27.0-d ^{233}Pa		94, 98, 312, 416	2-4 wks.	0.08	1.0
Zr	^{94}Zr	17.4	65-d ^{95}Zr$^{\beta}$	0.08	725, 757		70	>140
			35.3-d ^{95}Nb		766	few mo.	--	--
Hf	^{180}Hf	35.2	42.5-d ^{181}Hf	10	133, 482	1 mo.	0.6	0.9
Ta	^{181}Ta	99.99	115.1-d ^{182}Ta	21	68, 100, 1122	few mo.	0.1[c]	0.08[c]
Sb	^{121}Sb	57.25	2.8-d ^{122}Sb	6	566	1 wk.	--	--
	^{123}Sb	42.75	60-d ^{124}Sb	3.3	1691	few mo.	0.6	0.6

Table 1. Production and properties of nuclides observable with Ge(Li) detectors.[a] (continued)

Element	Target isotope	Isotopic abundance (%)	Product nuclide	Effective $\sigma(n_{th},\gamma)$ (barns)	Best photopeak(s) used in determination (keV)	Best time after irradiation for counting	Sensitivity (ppm unless % indicated) G−2	W−1
Mn	^{55}Mn	100	2.58-h ^{56}Mn	13.3	847, 1811	few hrs.	12	25
Co	^{59}Co	100	5.26-y ^{60}Co	37	1173, 1332	few mo.	0.3	0.1
Fe[d]	^{58}Fe	0.31	45-d ^{59}Fe	1.1	1100, 1291	few mo.	200	700
Sc	^{45}Sc	100	83.9-d ^{46}Sc	23	889, 1120	few mo.	0.02	0.02
Cr	^{50}Cr	4.31	27.8-d ^{51}Cr	17	320	1 mo.	0.8	20

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[a] Isotopic abundances, half lives, and thermal-neutron cross sections are in general those given by Lederer, Hollander and Perlman (1967). These quantities are also summarized on the G. E. Chart of Nuclides.

[b] ^{24}Na may also be produced via ^{27}Al(n, α). This reaction may be an important source of ^{24}Na in rocks high in Al content and low in Na.

[c] Based on the high resolution spectra.

[d] One also observes the 835-keV line from 303-day ^{54}Mn produced by ^{54}Fe (n, p).

results indicate that the trace element data may be useful for distinguishing the ashes one from another.

The number of elements determined can be extended by modifying the procedure to some extent. Thus, copper could be determined by measuring 511-511 keV coincidences from the annihilation of $\beta+$ particles (Schmitt, *et al,* [3]).

A significant improvement in sensitivity is obtained by the use of an anti-Compton shield around the detector. Preliminary experiments show that by routing the "normal" spectrum to one half of the analyzer memory and the coincidence spectrum to the other, this allows the maximum of information to be obtained from this system.

Another powerful extension of the method arises from NaI(Tl)-Ge(Li) coincidence measurements. Any isotope which has cascade gamma rays could be studied with such a system and detection limits significantly lowered. This procedure has its main uses in the study of meteorites where abundances of many trace elements are considerably lower than in comparable terrestrial samples. The method will amost certainly be required in the study of lunar samples.

III. Acknowledgements

We would like to thank Dr. John A. Cooper of Battelle Memorial Institute, Richland, Washington for allowing us to use his facilities and for help in counting the samples.

IV. References

[1] Bowman, H. R., Hyde, E. K., Thompson, S. G., and Jared, R. C., Science **151,** 562-568 (1966).

[2] Brunfelt, A. O., and Steinnes, E., Geochim. Cosmochim. Acta **30,** 921-928 (1966).

[3] Schmitt, R. A., Smith. R. H., and Goles, G. G., J. Geophys. Res. **70,** 2419-2444 (1965).

[4] Stueber, A. M., and Goles, G. G., Geochim. Cosmochim. Acta **31,** 75-93 (1967).

AN INVESTIGATION OF TRACE ELEMENTS IN MARINE AND LACUSTRINE DEPOSITS BY MEANS OF A NEUTRON ACTIVATION METHOD

O. Landstrom and K. Samsahl

AB Atomenergi
Stockholm, Sweden

C. G. Wenner

Department of Quaternary Research
University of Stockholm
Stockholm, Sweden

I. Introduction

In the present work a neutron activation method suitable for multielemental analysis was applied in a study of the use of trace elements in distinguishing marine and lacustrine deposits in the Viskan Valley on the Swedish West Coast.

An extensive investigation of the different strata in this area was carried out by von Post [1] during the years 1932-1944 with the aim of making a graph of the shore fluctuations. The samples from this investigation were used in the present test. The Viskan Valley represents a limited area, where the mineral constituent of the sediments comes from geologically homogeneous surroundings. During a rather short time, less than 8,000 years, marine and fresh-water conditions have alternated several times. These changes are well defined as they have been based on paleontologic evidence in many sections of the valley, and represent movements of the shore well known in the Quaternary history of the Viskan Valley.

The series of samples which have been tested in the present work are numbered 629, 1511 and 16. They arise from three different sections of the Viskan Valley (Fig. 1) situated about 20, 30 and 35 km from the present coastline. In the two sections first mentioned, representing mainly sediments in deep water, the strata are in spite of different degrees of salinity similar as regards the size of mineral particles and the content of organic materials. The section with bore-hole 16, on the other hand, represents a part of the Viskan Valley located near the highest limit of the postglacial transgression during the younger sea-fiord stage.

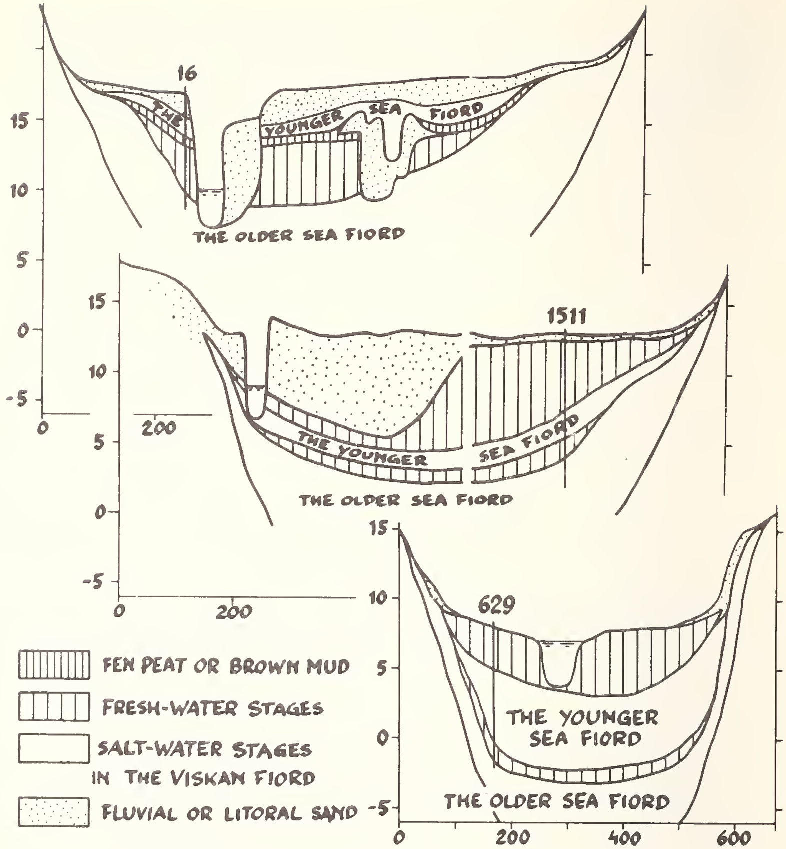

Figure 1. Sections of the Viskan Valley.

Attempts have been made to use B as a salinity indicator in two sequences of strata from the Viskan Valley [2]. In other regions one has tried to differentiate marine and fresh-water sediments by means of trace elements [3-4].

II. Experimental

A. CHEMICAL SEPARATION METHOD

Since Mn could be determined very easily by instrumental analysis, this was done in a first step using a short-time irradiation with a low thermal neutron flux. After the determination of Mn, the samples (about 15-20 mg) were reirradiated for about 3 days in a thermal flux of $2 \times 10^{13} \mathrm{n \cdot cm^{-2} \cdot sec^{-1}}$. After 1-2 day's decay, the radioactive constituents of the samples were separated into 20 groups with the chemical group separation method shown in Figure 2. The method, consisting mainly of the ion-exchange technique, is in principle the same as a routine procedure originally developed and used in neutron activation analysis of biological material [5]. However, the introduction of a few additional steps in the procedure were found necessary in the case of argillaceous samples.

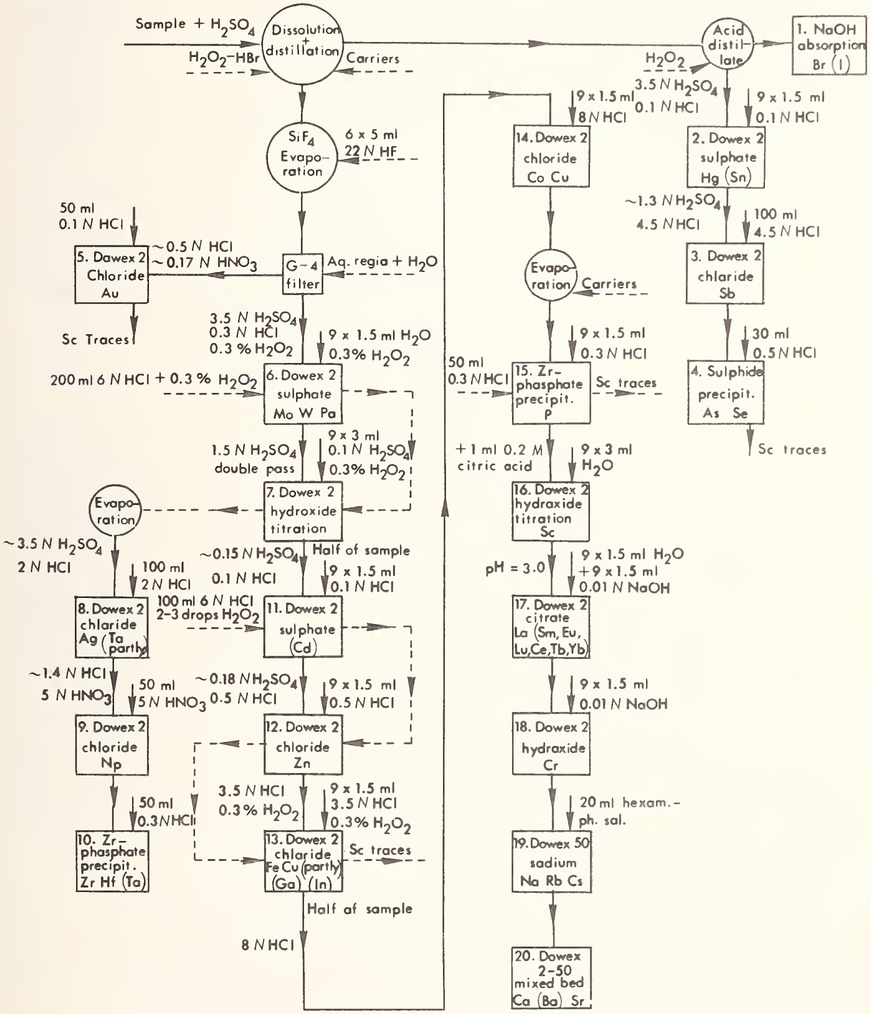

Figure 2. Chemical separation scheme.

One of these steps consists of the removal of silicic acid from the sample solutions by vaporizing SiF_4 from a mixture of H_2SO_4 and HF, after the initial division of the radioactive constituents of the sample into two main groups by means of distillation with H_2O_2 and HBr [6].

Also, additional washing steps were applied to some of the ion exchange columns and precipitates in the series. These steps remove excessive amounts of mainly scandium-46 activity (Fig. 2).

B. Measurement and Calculations

The identification of the separated radionuclides was performed by means of gamma-ray spectrometry, using a 3 in. × 3 in. well-type NaI detector connected to a multichannel analyzer.

The concentration of each element was calculated by comparing the activity of the different groups with that of simultaneously irradiated standards of known amounts [5].

Final values have been corrected when necessary for interferences due to fission products of uranium as well as for other interfering reactions. The correction for the activity introduced by fission products has been calculated in a way similar to that described by Loveridge, *et al* [7].

III. Results and Discussion

A. Results

The accuracy of the method was tested by analysis of the standard rock samples, G-1 and W-1. The average of two determinations are given in Table 1. In the same table are also given the values obtained from analysis of the biological standard (kale) distributed by Dr. Bowen.

Samples from bore-hole 629, representing four different depths and stages were analyzed and compared: 1.80 m fresh water in the present lake; 6.20 m salt water in the younger sea-fiord; 9.00 m fresh water in the ancient lake; and 9.80 m salt water in the older sea-fiord.

In order to determine the precision of the method, four analyses were made on samples from the 1.80 m depth. The mean of the four determinations is used for the comparison with the results from the other stages. Altogether 30 elements were quantitatively determined and the results are given in Table 2.

As a second step, some elements, namely Br, Hg, Mn, and Se, which seemed to show a difference in concentration between the marine and the fresh water layers were analyzed in some additional samples from borehole 629. As and Sb were also included as they could easily be analyzed simultaneously. The results are shown in Figure 3.

To verify the validity of the observations in Figure 3, the same elements, excluding Hg, were also analyzed in boreholes 1511 and 16 from two other sections. In this case, the irradiations had to be performed in a lower flux in the reactor, R1, and the activity of Hg was considered too low for a satisfactory determination. The results of these analyses are shown in Figures 4 and 5.

Table 1. Concentrations of elements determined in the standard rock samples G–1 and W–1 and in a biological standard (kale).

Element determined[a]	Nuclide used for the determination	G–1[b]	W–1[b]	Kale
Antimony	^{122}Sb	0.20	0.98	0.065 ± 0.006
Arsenic	^{76}As	0.52	1.7	0.11 ± 0.03
Bromine	^{82}Br	0.17	0.42	23 ± 1
Calcium %	^{47}Ca	0.94	7.5	4.2 ± 0.2
Cerium	^{141}Ce	130	24	0.18 ± 0.03
Cesium	^{134}Cs	1.2	0.8	0.069 ± 0.003
Chromium	^{51}Cr	14	105	0.18 ± 0.02
Cobalt	^{60}Co	2.7	43	0.052 ± 0.005
Europium	^{52}Eu	1.5	1.2	
Gallium	^{72}Ga	18	16	0.027 ± 0.001
Hafnium	^{181}Hf	5.6	3.4	<0.01
Iron %	^{59}Fe	1.3	8.0	0.012 ± 0.0003
Lanthanum	^{140}La	82	10.5	0.08 ± 0.01
Lutetium	^{177}Lu	0.16	0.51	
Manganese	^{56}Mn	170	1175	14.0 ± 1
Mercury	^{203}Hg	0.12	0.33	0.14 ± 0.01
Rubidium	^{86}Rb	224	22	50 ± 3
Samarium	^{153}Sm	7.4	4.1	0.16 ± 0.008
Scandium	^{46}Sc	2.9	37	0.0087 ± 0.0007
Selenium	^{75}Se	<0.1	0.17	0.15 ± 0.01
Sodium %	^{24}Na	2.34	1.52	0.216 ± 0.008
Strontium	^{85}Sr	246	186	95 ± 4
Tantalum	^{182}Ta	1.5	0.4	<0.05
Terbium	^{160}Tb	0.43	0.82	
Thorium	^{233}Pa	33	1.9	0.0092 ± 0.0010
Tungsten	^{187}W	0.4	0.5	0.057 ± 0.007
Uranium	^{239}Np	2.7	0.53	0.0081 ± 0.0012
Ytterbium	^{175}Yb		1.5	
Zinc	^{65}Zn	43	92	32 ± 1
Zirconium	^{95}Zr	202	105	

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[a] In ppm except where indicated as %.

[b] Average of 2 determinations.

B. Discussion

The reliability of decomposing the samples with a mixture of sulfuric acid and hydrogen peroxide prior to the distillation procedure was checked as follows:

Table 2. Concentrations of elements in bore hole 629.

	Depth in meter				
Element determined[a]	1.80 Present lake mean		6.20 Younger sea–fiord	9.00 Ancient lake	9.80 Older sea–fiord
Antimony	0.47 0.52 0.48 0.50	0.49 ± 0.02	0.63	0.41	0.48
Arsenic	4.1 4.2 4.2 4.8	4.3 ± 0.32	8.2	5.8	5.5
Bromine	5.9 6.7 6.3 7.7	6.7 ± 0.77	131	18	21
Calcium %	0.72 1.06 1.10 0.99	0.97 ± 0.17	2.1	1.2	2.8
Cerium	230 250 284 207	243 ± 32	207	192	210
Cesium	6.6 7.3 6.3 7.0	6.8 ± 0.44	4.7	7.0	7.3
Chromium	48 58 51 54	53 ± 4.3	47	57	70
Cobalt	21 22 22 20	21 ± 1.0	11	20	20
Europium	2.4 3.0 2.5 2.2	2.5 ± 0.34	2.2	3.3	2.7

Table 2. Concentrations of elements in bore hole 629 (continued).

	Depth in meter				
Element determined	1.80 Present lake	mean	6.20 Younger sea–fiord	9.00 Ancient lake	9.80 Older sea–fiord
Gallium	14 17 13 17	15 ± 2.1	17	13	18
Hafnium	5.4 5.7 6.3 6.6	6.0 ± 0.55	4.7	6.4	6.6
Iron %	5.8 7.1 6.0 6.1	6.2 ± 0.58	5.8	7.1	6.5
Lanthanum	57 59 53 53	56 ± 3.2	55	70	60
Lutetium	0.89 1.08 1.03 0.80	0.95 ± 0.13	0.6	1.3	1.3
Manganese %	0.130 0.127 0.128 0.129	0.128 ± 0.0014	0.058	0.109	0.059
Mercury	0.36 0.36 0.39 0.33	0.36 ± 0.025	2.0	0.81	1.4
Rubidium	109 117 110 115	113 ± 3.9	90	129	145
Samarium	15 18 13 14	15 ± 2.2	15	20	13

Table 2. Concentrations of elements in bore hole 629 (continued).

	Depth in meter				
Element determined	1.80 Present lake mean		6.20 Younger sea–fiord	9.00 Ancient lake	9.80 Older sea–fiord
Scandium	14 17 14 15	15 ± 1.4	10	13	15
Selenium	0.68 0.78 0.75 0.67	0.72 ± 0.053	2.0	1.0	0.32
Sodium %	1.11 1.17 1.16 1.16	1.15 ± 0.027	0.96	1.43	1.39
Strontium	81 116 131 132	115 ± 24	160	191	217
Tantalum	1.16 1.43 1.04 1.25	1.2 ± 0.17	1.2	1.0	–
Terbium	0.84 1.13 0.88 0.93	0.95 ± 0.13	1.1	1.5	1.6
Thorium	14 14 16 13	14 ± 1.3	12	15	15
Tungsten	1.5 1.6 1.5 1.5	1.5 ± 0.058	1.2	1.6	1.6
Uranium	6.1 6.3 6.3 6.5	6.3 ± 0.16	4.8	11.2	4.7

Table 2. Concentrations of elements in bore hole 629 (continued).

		Depth in meter			
Element determined		1.80 Present lake mean	6.20 Younger sea–fiord	9.00 Ancient lake	9.80 Older sea–fiord
Ytterbium	1.9 2.8 2.4 2.9	2.5 ± 0.45	1.9	2.9	3.1
Zinc	116 122 120 112	118 ± 4.5	87	143	117
Zirconium	295 349 264 327	309 ± 37	253	423	230

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[a] In ppm except where indicated as %.

Irradiated samples were dissolved in a few ml of water after fusion with Na_2O_2 and NaOH at 600 °C. The solution, containing added carriers in an amount corresponding to 5 mg each of As, Br, Hg, Sb and Se, was strongly acidified with H_2SO_4 and the elements were finally distilled [6]. The activity in the distillate was, except Hg, in full agreement with those obtained with the sulfuric acid method. Regarding Hg, lower values were obtained after a Na_2O_2 attack, probably owing to volatilization during the fusion process. However, the main reason for using a mixture of H_2SO_4 and H_2O_2 as a decomposing agent in the present work was to keep the salt concentration down in the solutions used for the subsequent ion exchange separation steps.

To determine whether elements other than silicon were vaporized, completely or in part during the hydrofluoric acid treatment special tests were carried out with activated samples as well as with inactive samples with added radionuclides. The experiments showed that traces of all the nondistillable elements determined in the present work were retained to more than 98 per cent in the sulphuric acid solution.

The results of the activation analysis are compared to the geologic development and to the properties of the various strata (Figs. 3, 4 and 5). Fossils were studied to establish whether each stratum represented a sea or lake deposit (Fig. 1). Among macrofossils shells of Mollusca have been used as salinity indicators; and among microfossils, especially, the diatoms.

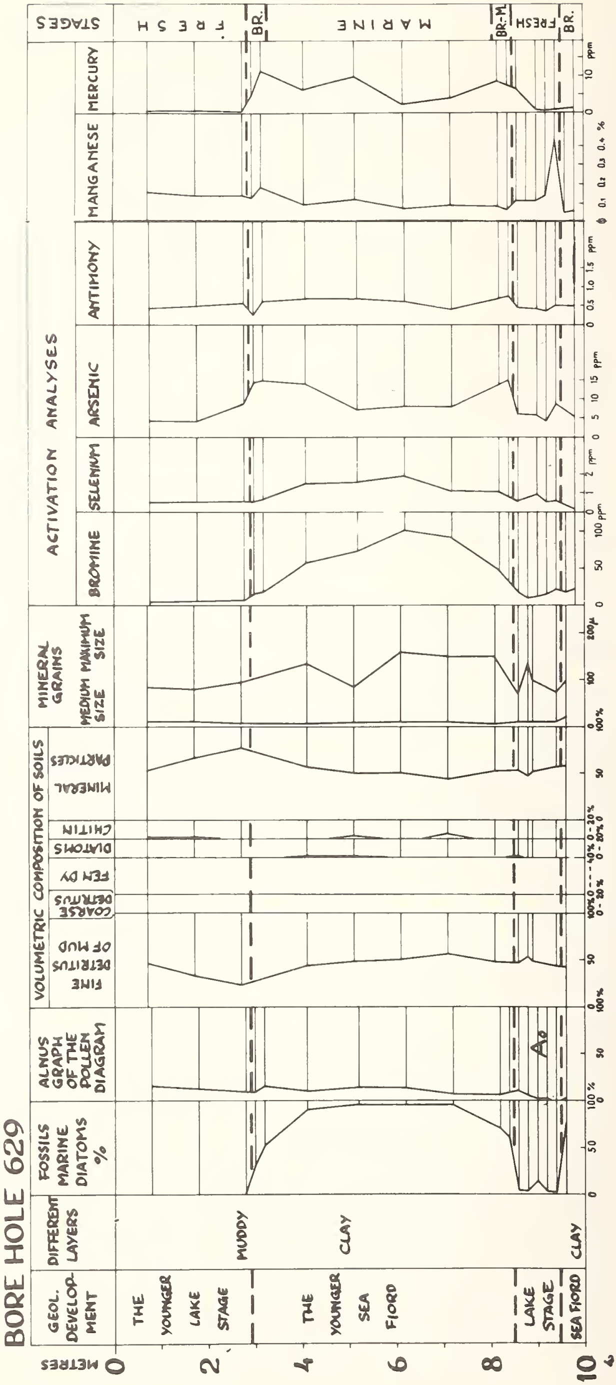

Figure 3. Concentration of selected trace elements in bore hole 629.

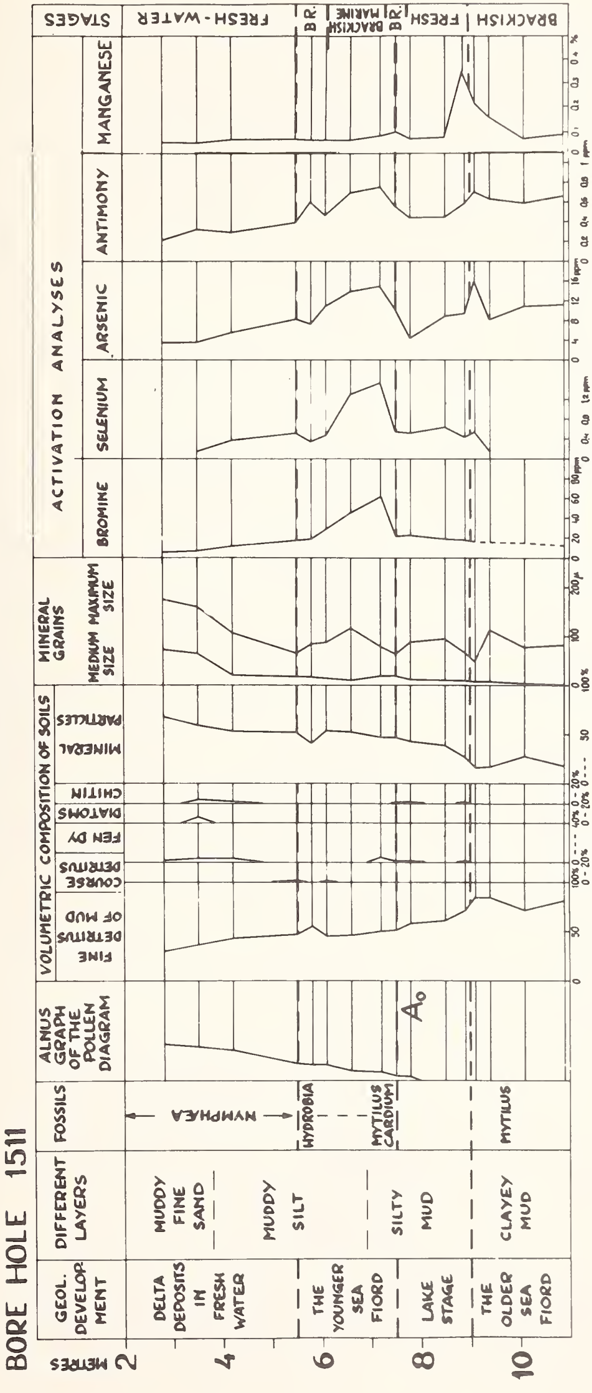

Figure 4. Concentration of selected trace elements in bore hole 1511.

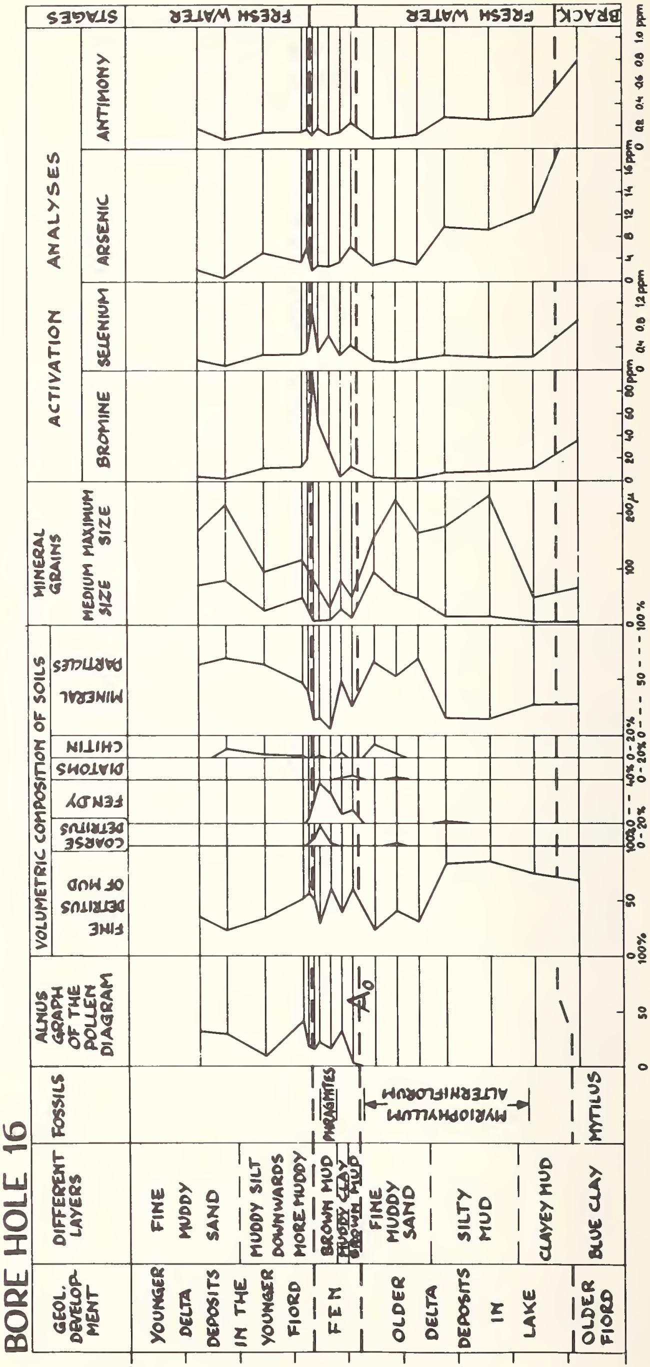

Figure 5. Concentration of selected trace elements in bore hole 16.

To check that the fresh water layer of the older lake is synchronous in the three sections, pollen analysis has been used. The beginning of the Alnus graph (A_0, representing the oldest occurrence of alder) represents a synchronous level in the older fresh water layer before the transgression which left the marine layer of the younger sea-fiord. The A – level in the Viskan Valley has been radiocarbon dated to 6,500 B.C. [8].

In order to supplement the ocular classification of layers, their percentage compositions (fine detritus, coarse detritus, dy (humus flocculation), diatom shells, chitin, mineral particles and medium and maximum sizes of the mineral grains) were determined according to a microscopic method [9].

From statistical treatment of the results [10] the following hypotheses may be stated: In the most marine layer of the post-glacial transgression, bromine has significantly higher values than in all other layers. Probably Br is also higher in the brackish marine layer compared to lacustrine and brackish layers. Arsenic does not show any certain trend with increasing salinity, antimony is significantly higher in the brackish marine layer than in the brackish layer of the younger sea-fiord and the fresh-water layer of the ancient lake. Selenium is higher in the marine layer than in the layer of the older sea-fiord and the fresh water layers. According to bore-hole 1511 there is also a difference between brackish-marine and brackish layers. Probably both the marine and the brackish-marine layers have higher amounts of Se than all other layers.

Disregarding the special and complicated sequence of strata in borehole 16, Br and Se are of interest as saline indicators in argillaceous layers with organic detritus. In the investigated sections of the Viskan Valley Br and Se have been enriched in the younger sea-fiord layers. But concerning the older sea-fiord layers with ferrous sulphide indicating stagnant water, the analyzed samples are few and the results contradictory. Possibly Br and Se were initially concentrated and later released by processes in the bottom below stagnant water.

For comparisons of trace element concentrations in rocks, soils, animals, plants and sea-water reference is made to Bowen's new collation and the literature cited by him [11].

According to this publication, Br can be very much enriched in marine, plants and animals. This is interesting, as remnants of organisms constitute the organic fine detritus of the argillaceous sediments.

IV. References

[1] von Post, L., Geol. Foren. i Stockholm. Forhandl. **60**, No. 3, (1938).

[2] Landergren, S., Arkiv f. kemi, mineral. och geol. **19**, No. 26, (1945).

[3] Keith, M. L., and Degens, E. T., Geochemical Indicators of Marine and Fresh-water Sediments, Researches in Geochem. by P. H. Abelson, John Wiley, New York, 1959, p. 38.

[4] Potter, P. E., Shimp, N. F., and Witters, J., Geochim. et Cosmochim. Acta **27,** 669 (1963).
[5] Samsahl, K., Brune, D., and Wester, P. O., Intern. J. Appl. Radiation Isotopes **16,** 273 (1965).
[6] Samsahl, K., Anal. Chem. **39,** 1480 (1967).
[7] Loveridge, B. A., Webster, R. K., *et al,* Anal. Chem. Acta **23,** 154 (1960).
[8] Wenner, C. G., Inqua-kongressen i Polen, Geol. Foren. i Stockholm Forhandl. **84,** No. 2, (1962).
[9] Lundqvist, G., Bodenablagerungen und Entwicklungstypen der Seen, Binnengewasser, Vol. 2, Stuttgart, 1927.
[10] Scheffe, H., The Analysis of Variance, Wiley and Sons, New York, 1959.
[11] Bowen, H. J. M., Trace Elements in the Biochemistry, Academic Press, New York, 1966.

GEOCHEMICAL SURVEYING BY MEANS OF NEUTRON ACTIVATION ANALYSIS WITH POSSIBLE APPLICATION TO CONTINENTAL DRIFT STUDIES

Ernst A. Uken[1], Gabriel G. Santos[2] and Richard E. Wainerdi

Activation Analysis Research Laboratory
College of Engineering
Texas A & M University
College Station, Texas

I. Introduction

In 1912, Alfred Wegner formulated a continental-drift theory [1], which was essentially a jigsaw puzzle fit of the existing continents to form a single unit which he called "Pangeae". Many detailed correlations [1-2] drawn from geology and palaentology indicate a common historical record of regions at opposite sides of the Atlantic.

The discovery of rifts along the mid-oceanic ridges has led to modern speculation that the ocean floor is continuously spreading, carrying the continents with it. Recent techniques have enabled researchers in palaeomagnetism to remove secondary magnetization, so that the ancient direction of the Earth's field may be determined unambiguously. This development has also led to confirmation of the continental-drift theory.

A computerized "least squares" criterion for fit developed by Sir Edward Bullard [3] and co-workers demonstrated that the best fit of the continents as shown in Figure 1 is along the 500 fathom contour.

Comparing radiometric ages of rocks from different continents, Hurley [4-5] and collaborators, found the correlation shown in Figure 2. They mention that the region near Sao Luis is probably part of an African craton left stranded on the coast of Brazil. A good agreement was also found between the structural trends of rocks from previously matching regions.

The present state of the art is summarized by Stubbs [6] as follows: "Having established the reality of continental drift, rock magnetists are now exploring just how the world's land masses were formerly connected and when they split apart".

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[1] On assignment from the South African National Institute for Metallurgy, Johannesburg.

[2] On assignment from the Philippine Atomic Energy Commisssion, Manila; NAS-IAEA Fellow.

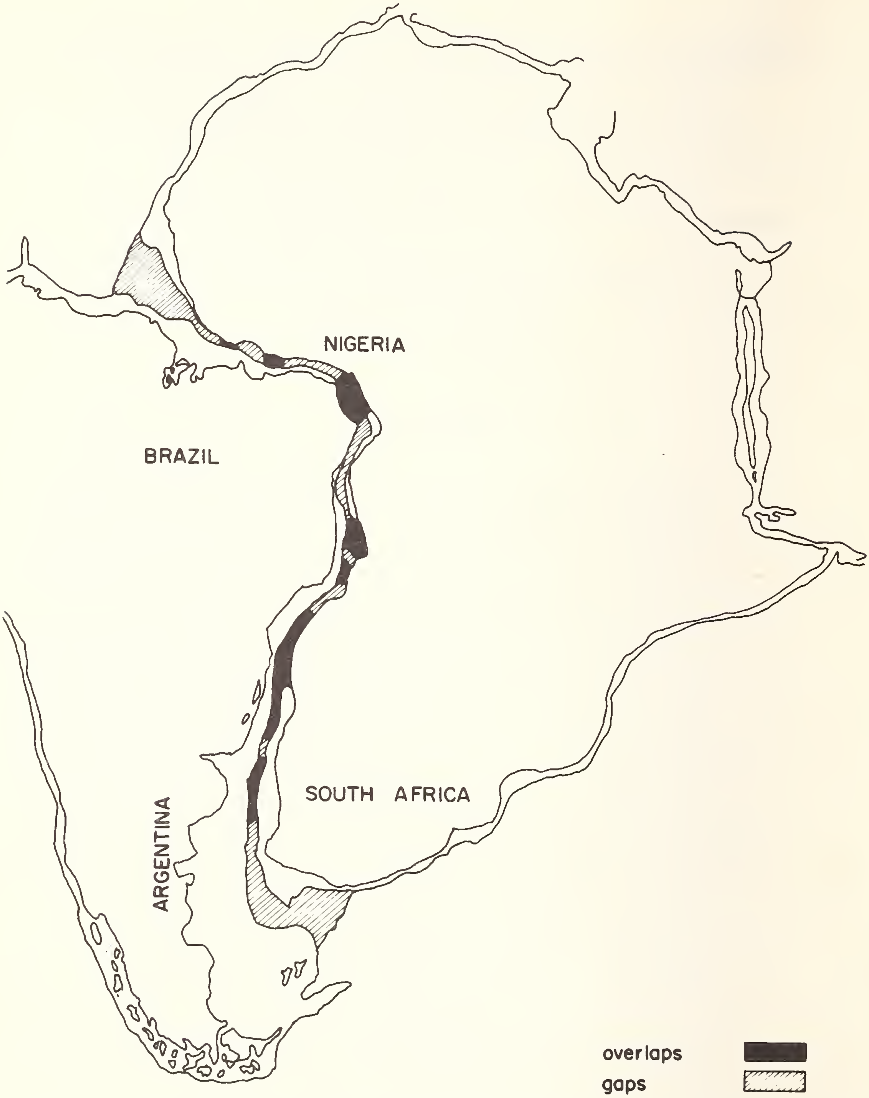

Figure 1. Least squares fit of the shelves of Africa and South America, by Sir E. Bullard.

Another approach, one that may particularly employ activation analysis techniques, would be the comparison of elemental abundances of supposedly contiguous regions, and the areal mapping of continuity of trace element occurrences.

II. Theoretical

A suitable way of determining the similarity of rocks is by the study of "metallogenic provinces". The latter may be defined as an area

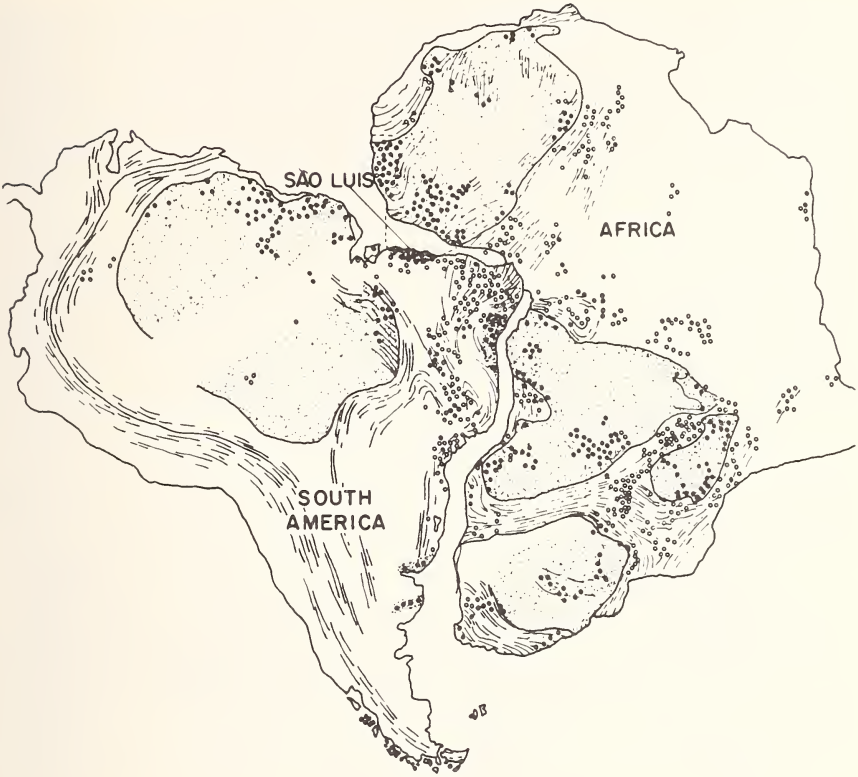

Figure 2. Matching geological age provinces of Africa and South America, by P. M. Hurley (1968).

characterized by a conspicuous concentration of a certain element or group of elements, as compared with other areas. Russian geologists [7-8] have successfully applied the concept of metallogenesis in geochemical exploration.

Burnham [9] showed that the trace element concentration of sulfides in the southwestern United States and northern Mexico could be contoured over an area of several thousand square miles. He also analyzed for Ag, Bi, Cd, Co, Ga, Mn, Mo, Ni, Sn, Fe and Sb in chalcopyrites and sphalerites from many ore deposits of this area. Rose [10] carried this investigation further, and concluded that on a regional basis both areas under consideration, *i.e.* Central District (New Mexico) and Bingham District (Utah) showed groupings defined by similar geographic location, trace element content, and geology.

Schuiling [11] plotted the economic and uneconomic occurrences of the element tin on "Pangeae". He used over 500 references and obtained "tin belts" across the Americas, Africa and Europe, as shown in Figure 3. These belts not only render support to the continental-drift theory, but also provide an indication of the potential use of such information to prospectors. There is reason to believe that the other trace elements may

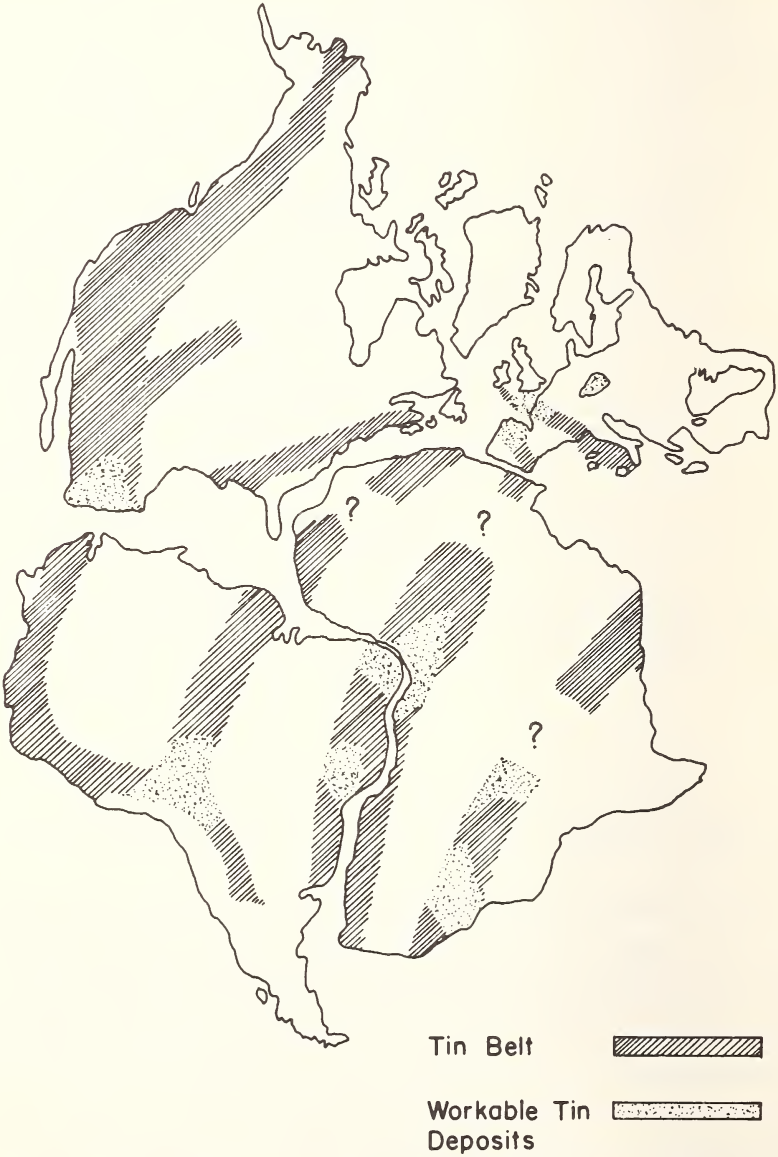

Figure 3. Tin belts across "Pangeae", by R. D. Schuiling (1967).

similarly render useful information both for precontinental-drift alignment purposes, and for economic geological purposes.

It was, therefore, felt that it would be worthwhile to investigate the feasibility of applying activation analysis to geological mapping procedures.

III. Experimental

The Enchanted Rock Batholith near Llano, Texas, was chosen as an initial candidate for mapping. Apart from being accessible, this area has been adequately mapped and substantial geological [12] and analytical [12-14] data are available. The granites encountered are also sufficiently average in composition so that some deductions may be made regarding the applicability of the methodology [15] to other locations.

Ten, thirty pound, fresh granite samples were taken from the surface of the batholith itself, at positions 1 to 10, as indicated in Figure 4. A further nine samples were taken at random outside the batholith, at positions cited in Table 3, so that an overall distance of approximately fifty miles could be considered.

Three chips weighing approximately 1 gram each were broken off at opposite ends of each sample. These whole rock fragments were then weighed, encapsulated, and, without any further sample preparation, were irradiated for 2 hours in Texas A&M Research Reactor at a thermal neutron flux of approximately $2 \times 10^{12} \mathrm{n \cdot cm^{-2} \cdot sec^{-1}}$. Samples of the standard granite rock "G-2" were also included to serve as reference standards.

Preliminary investigations [15] revealed that the interfering activity of sodium-24 is negligible after a decay period of 14 days. The induced gamma-ray activity of all samples was therefore measured 14 days and 40 days after the end of irradiation. A 19 $\mathrm{cm^3}$ lithium drifted germanium detector was used in conjunction with a Victoreen 3200 channel analyzer to perform the gamma-ray spectral measurements.

IV. Results and Discussion

A. RESULTS

In Figure 5 examples of the observed spectra are shown as measured over a counting period of 60 minutes analyzer live-time and a decay period of 40 days. The various species were identified by conventional methods. The rates of peak decay and secondary peak energies were also used to confirm the isotopes listed in Table 1.

The areas of the gamma-ray peaks given in Table 1 were calculated by an adapted version of Covell's method [16], to yield quantitative values

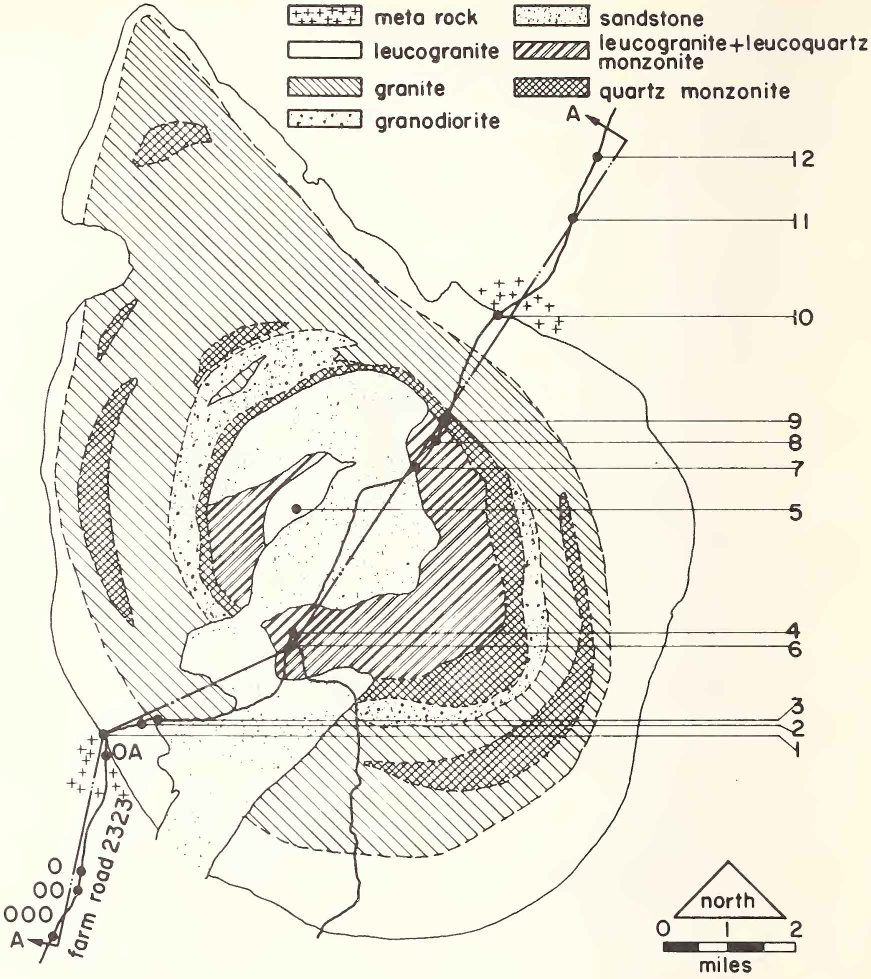

Figure 4. Sampling sites along a diametric traverse of the Llano Enchanted Rock Batholith, Texas.

for Fe, Sc, Co, La, Eu, Hf and Ta. All concentrations were calculated relative to the values obtained by Gordon, *et al* [17], for the standard granite rock "G-2", shown in Table 2.

After correcting for neutron flux variations and normalizing to a sample weight of 1 gram and decay times of 14 days and 40 days respectively, the values given in Table 3 were obtained.

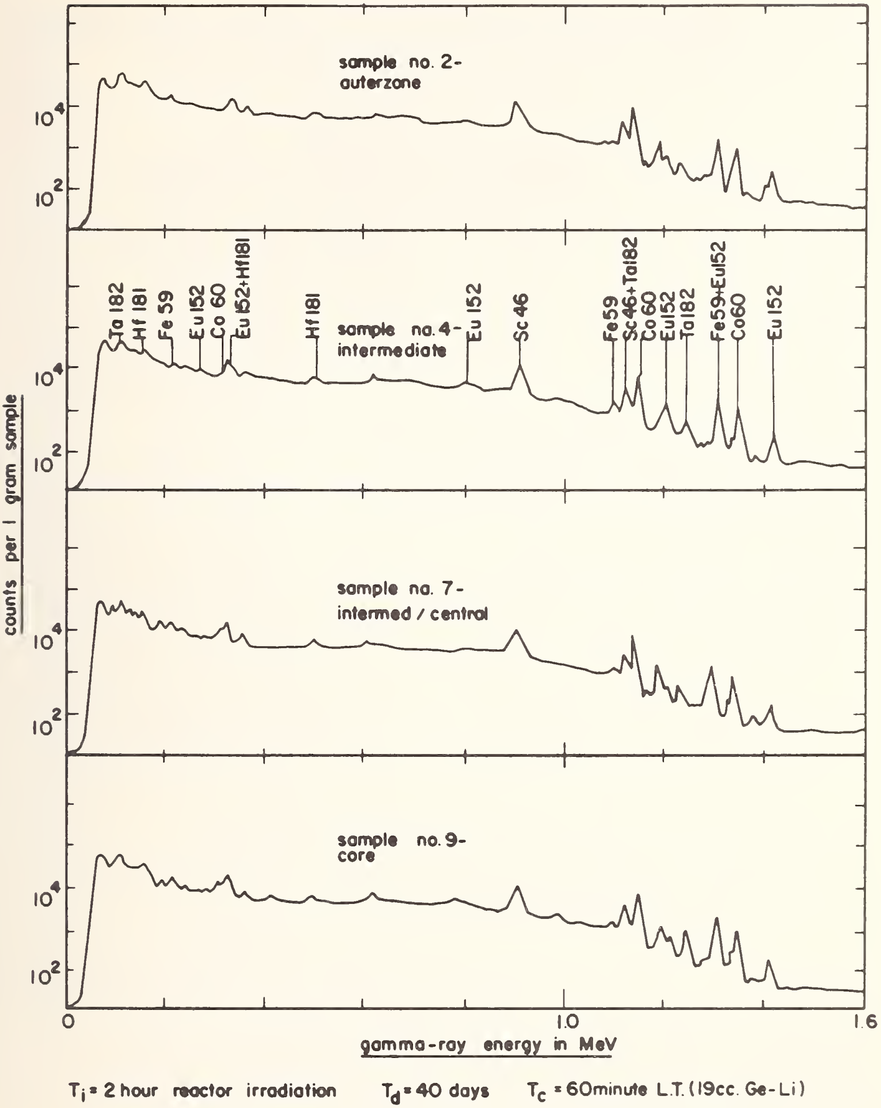

Figure 5. Comparison of spectra from four different Llano granites.

B. Discussion

Figures 6 and 7 indicate that the symmetry of the elemental trends are in agreement with generally accepted and mapped nearly concentric zonal arrangement of the various rock types shown in Figure 4. It must be noted that any unusual or anomalous elemental trends could have been easily

Table 1. Identification of gamma-ray energies emitted by Llano samples, after a 2–hour reactor neutron irradiation.

Isotope	Half life	Decay time (days)	Gamma-ray energies chosen (keV)	Comments
^{59}Fe	45 d	14	1100	Interference from ^{152}Eu <5%
^{46}Se	83.9 d	14	889	Resolved from the Compton edges of the 1120 keV, ^{46}Sc peak and
^{60}Co	5.26 y	40	1330	No known interference
^{140}La	40.2 h	14	1600	No known interference
^{152}Eu	12 y	40	1406	No known interference
^{181}Hf	42.5 d	40	480	Resolved from the 490 keV ^{140}La peak
^{182}Ta	115.1 d	40	1221	Resolved from the 1212 keV ^{152}Eu peak.

Table 2. Calibration as based on values of standard granite rock sample "G–2".

Element	Concentration[a]	Observed gamma-ray activity counts/h/g
Iron	1.72 ± 0.05 %	1,778
Scandium	3.5 ± 0.2 ppm	21,934
Cobalt	4.3 ± 0.2 ppm	372
Lanthanum	81.0 ± 1.0 ppm	4,701
Europium	1.37 ± 0.05 ppm	236
Hafnium	7.8 ± 0.5 ppm	3,470
Tantalum	1.0 ± 0.2 ppm	147

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[a] See reference [19].

Table 3. Analytical results of uncrushed Llano samples.

Sample									
Number	Distance from center of pluton miles	Rock type	Iron	Scandium (ppm)	Cobalt (ppm)	Lanthanum (ppm)	Europium (ppm)	Hafnium (ppm)	Tantalum (ppm)
000	10 SW	Shale	0.28 ± 0.02	3.4 ± 0.3	3.4 ± 0.3	11.9 ± 0.3	0.6 ± 0.1	1.7 ± 0.2	0.4 ± 0.1
00	9 SW	Limestone	0.25 ± 0.02	1.4 ± 0.3	2.3 ± 0.3	4.3 ± 0.1	0.5 ± 0.1	1.1 ± 0.1	0.5 ± 0.1
0	8½ SW	Meta Sediment	0.63 ± 0.02	1.6 ± 0.3	1.2 ± 0.2	10.9 ± 0.3	0.6 ± 0.1	3.0 ± 0.2	0.5 ± 0.1
0A	6½ SW	Meta Sediment	0.82 ± 0.3	2.6 ± 0.3	0.9 ± 0.2	18.7 ± 0.5	1.1 ± 0.1	5.4 ± 0.3	0.7 ± 0.2
1	6 SW	Leucogranite	1.72 ± 0.06	0.8 ± 0.1	0.6 ± 0.1	31.8 ± 0.6	1.2 ± 0.1	2.8 ± 0.2	0.6 ± 0.1
			1.45 ± 0.06	1.2 ± 0.2	1.3 ± 0.2	36.5 ± 0.7	0.8 ± 0.1	3.1 ± 0.2	0.6 ± 0.1
			1.19 ± 0.05	1.4 ± 0.3	0.9 ± 0.2	31.4 ± 0.6	1.1 ± 0.1	2.2 ± 0.2	0.8 ± 0.2
2	5½ SW	Leucogranite	1.76 ± 0.06	2.4 ± 0.3	1.0 ± 0.2	23.8 ± 0.5	1.1 ± 0.1	4.4 ± 0.3	0.9 ± 0.2
			2.16 ± 0.07	2.8 ± 0.3	1.9 ± 0.2	29.2 ± 0.6	1.2 ± 0.1	4.6 ± 0.3	0.8 ± 0.2
			2.00 ± 0.07	3.3 ± 0.3	1.5 ± 0.2	27.2 ± 0.6	1.2 ± 0.1	3.1 ± 0.3	0.9 ± 0.2
3	5 SW	Granite	2.44 ± 0.07	7.0 ± 0.3	1.8 ± 0.2	58.8 ± 0.8	1.1 ± 0.1	6.6 ± 0.4	1.2 ± 0.2
			2.14 ± 0.07	0.7 ± 0.1	2.0 ± 0.2	23.0 ± 0.5	1.0 ± 0.1	4.9 ± 0.3	0.7 ± 0.1
			2.49 ± 0.07	3.6 ± 0.3	1.7 ± 0.2	56.2 ± 0.8	1.2 ± 0.1	3.6 ± 0.3	0.7 ± 0.1
4	2 SW	Leucoquartz monzonite	3.45 ± 0.08	5.2 ± 0.3	3.3 ± 0.3	37.9 ± 0.7	1.2 ± 0.1	4.6 ± 0.3	1.4 ± 0.2
			3.23 ± 0.08	3.7 ± 0.3	2.9 ± 0.3	23.0 ± 0.5	1.3 ± 0.5	3.5 ± 0.3	0.9 ± 0.2
			3.09 ± 0.08	4.6 ± 0.3	2.5 ± 0.3	33.4 ± 0.6	1.1 ± 0.1	5.7 ± 0.3	1.0 ± 0.2
6	2 SW	Leucoquartz monzonite	2.61 ± 0.07	3.9 ± 0.3	2.5 ± 0.3	16.9 ± 0.5	1.3 ± 0.1	3.9 ± 0.3	1.1 ± 0.2
			2.87 ± 0.07	5.2 ± 0.3	2.7 ± 0.3	20.6 ± 0.5	1.2 ± 0.1	4.4 ± 0.3	1.2 ± 0.2
			2.88 ± 0.07	4.4 ± 0.3	2.7 ± 0.3	17.3 ± 0.5	1.3 ± 0.1	4.4 ± 0.3	1.3 ± 0.2

Table 3. Analytical results of uncrushed Llano samples (continued).

Sample									
Number	Distance from center of pluton miles	Rock type	Iron	Scandium (ppm)	Cobalt (ppm)	Lanthanum (ppm)	Europium (ppm)	Hafnium (ppm)	Tantalum (ppm)
5	0	Leucogranite	2.54 ± 0.07	3.0 ± 0.3	2.1 ± 0.3	20.4 ± 0.5	0.8 ± 0.1	2.4 ± 0.2	0.7 ± 0.2
			2.59 ± 0.07	3.3 ± 0.3	1.9 ± 0.2	27.6 ± 0.6	0.9 ± 0.1	2.7 ± 0.2	0.7 ± 0.2
			2.24 ± 0.07	3.3 ± 0.3	1.7 ± 0.2	26.1 ± 0.6	0.6 ± 0.1	3.2 ± 0.3	0.6 ± 0.2
7	2 NE	Leucoquartz monzonite	2.88 ± 0.07	4.1 ± 0.3	3.6 ± 0.3	46.4 ± 0.7	1.0 ± 0.1	4.8 ± 0.3	1.1 ± 0.2
			3.12 ± 0.08	4.6 ± 0.3	3.6 ± 0.3	56.3 ± 0.9	1.0 ± 0.1	3.5 ± 0.3	1.4 ± 0.2
			2.75 ± 0.07	4.7 ± 0.3	3.9 ± 0.4	50.0 ± 0.8	1.2 ± 0.1	4.1 ± 0.3	1.1 ± 0.2
8	2½ NE	Leucoquartz monzonite	2.37 ± 0.07	4.0 ± 0.3	3.3 ± 0.3	31.1 ± 0.6	1.1 ± 0.1	4.2 ± 0.3	1.3 ± 0.2
			2.24 ± 0.07	4.0 ± 0.3	2.4 ± 0.3	38.9 ± 0.7	1.2 ± 0.1	3.8 ± 0.3	1.2 ± 0.2
			2.62 ± 0.07	4.0 ± 0.3	3.0 ± 0.3	33.2 ± 0.6	1.0 ± 0.1	4.8 ± 0.3	1.5 ± 0.2
9	3 NE	Quartz monzonite	2.67 ± 0.07	3.2 ± 0.3	2.1 ± 0.2	51.7 ± 0.8	1.5 ± 0.2	5.9 ± 0.3	1.4 ± 0.2
			2.64 ± 0.07	3.1 ± 0.3	2.6 ± 0.3	50.3 ± 0.8	1.3 ± 0.1	6.2 ± 0.3	1.4 ± 0.2
			2.94 ± 0.07	3.8 ± 0.3	3.1 ± 0.3	51.0 ± 0.8	1.3 ± 0.1	5.5 ± 0.3	1.7 ± 0.3
10	5 NE	Leucogranite	1.48 ± 0.06	2.1 ± 0.3	1.5 ± 0.2	88.8 ± 0.2	1.5 ± 0.2	6.5 ± 0.4	1.5 ± 0.2
			2.08 ± 0.07	2.3 ± 0.3	1.5 ± 0.2	100.3 ± 2.5	1.9 ± 0.2	6.5 ± 0.4	1.0 ± 0.2
			1.81 ± 0.06	2.4 ± 0.3	1.6 ± 0.2	78.1 ± 1.6	1.7 ± 0.2	6.9 ± 0.4	1.4 ± 0.2
11	7 NE	Leucogranite	3.10 ± 0.08	2.3 ± 0.3	1.0 ± 0.2	39.6 ± 0.7	0.7 ± 0.1	3.0 ± 0.3	1.1 ± 0.2
12	8 NE	Leucogranite	3.89 ± 0.09	3.3 ± 0.3	1.1 ± 0.2	50.5 ± 0.8	0.5 ± 0.1	3.4 ± 0.3	0.9 ± 0.2
13	13 NE	Granite	2.21 ± 0.07	1.2 ± 0.2	0.7 ± 0.1	45.7 ± 0.7	0.8 ± 0.1	3.4 ± 0.3	1.1 ± 0.2
14	14 NE	Leucoquartz monzonite	2.47 ± 0.07	2.0 ± 0.3	1.7 ± 0.2	23.0 ± 0.6	0.8 ± 0.1	2.1 ± 0.2	1.5 ± 0.2
15	37 NE	Orthoclase–biotite hornfels	3.56 ± 0.08	8.1 ± 0.4	4.0 ± 0.3	25.3 ± 0.6	0.6 ± 0.1	2.9 ± 0.2	1.6 ± 0.3

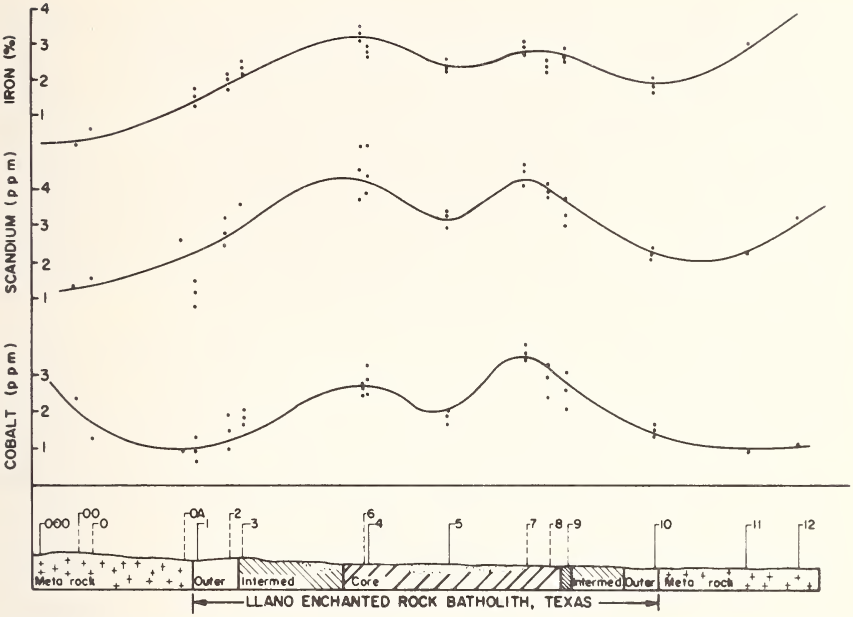

Figure 6. Distribution of iron, scandium and cobalt across the Llano Enchanted Rock Batholith, Texas.

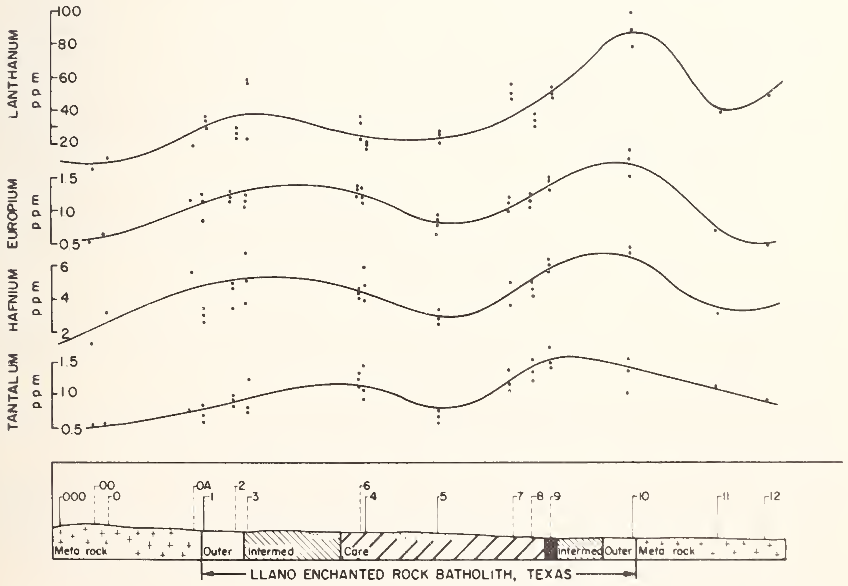

Figure 7. Distribution of lanthanum, europium, hafnium and tantalum across the Llano Enchanted Rock Batholith, Texas.

detected if they were present. In addition, it may be added that the above element concentrations are similar to that of the standard granite "G-2".

Furthermore, the compositional trends as shown in Figures 6 and 7 appear to extend beyond the pluton boundary irrespective of the host rock type. The geological explanation and significance is given elsewhere [18,19], but may it suffice here to conclude that the method outlined may provide useful data to: (a) Substantiate the concepts of metallogenesis, (b) Render support to the still somewhat controversial continental-drift theory, and (c) Enable large scale mineral exploration to be extended to inaccessible and relatively unmapped regions.

V. References

[1] Wegener, A., The Origin of Continents and Oceans. Translation from German by J. Biram, Dover Publication, Inc., New York, 1966.

[2] du Toit, A. L., A Geological Comparison of South America with South Africa, Carnegie Institution of Washington, Publ. No. 381, Washington, 1927.

[3] Bullard, Sir E., Phil. Trans. of the Royal Soc. **258,** 41 (1965).

[4] Hurley, P. M., *et al,* Science **157,** 3788 (1967).

[5] Hurley, P. M., Scien. Am. **218,** 53 (1968).

[6] Stubbs, P., New Scientist, pp. 126-127, April 1968.

[7] Bryner, L., Mining Eng. **15,** 59 (1963).

[8] Bilibin, Y. A., Gosgeolteknizdat, 1955. Dept. of the Secretary of State of Canada, Foreign Languages Div, Bureau of Translations, No. 58972.

[9] Burnham, C. W., N. Mex. Bur. Mines and Mineral Res. Bull. 65, 1959.

[10] Rose, A. W., Geochim. Cosmochim. Acta **31,** 547 (1967).

[11] Schuiling, R. D., Econ. Geol. **62,** (1967).

[12] Hutchinson, R. M., Geol. Soc. America Bull. **67,** (1956).

[13] Billings, G. K., Ph.D. Thesis, Rice University, (1963).

[14] Ragland, P. C., Billings, G. K., and Adams, J. A. S., "Magmatic Differentiation and Autometasomatism in a Zoned Granite Batholith from Central Texas, USA" (To be published, 1968).

[15] Uken, E. A., Santos, G. G., Yule, H. P., and Wainerdi, R. E., "Multi-Elemental Ratios Obtained by Neutron Activation Analysis for a Study of the Continental Drift Theory", Presented at the Pacific Conference on Chemistry and Spectroscopy, Anaheim, Calif., October 1967.

[16] Covell, D. F., Anal. Chem. **31,** 1785 (1959).

[17] Gordon, G. E., *et al,* Instrumental Activation Analysis of Standard Rocks with High-Resolution Gamma-Ray Detectors, Geochim. Cosmochim. Acta **32,** 369 (1968).

[18] Uken, E. A., Geological Mapping by Neutron Activation Analysis, South African Assoc. for the Advancement of Science 66th Congress, Lourenco Marques, July 1968.

[19] Wainerdi, R. E., Uken, E. A., Santos, G. G., and Yule, H. P., Neutron Activation Analysis and High Resolution Gamma-Ray Spectrometry Applied to Areal Elemental Distribution Studies, I.A.E.A. Meeting on Use of Nuclear Techniques in the Prospecting and Development of Mineral Resources, Lima, Nov. 1968.

VOLCANOLOGICAL STUDIES USING ACTIVATION ANALYSIS TECHNIQUES

Gabriel Santos [1] **and Richard E. Wainerdi**

Activation Analysis Research Laboratory
Texas A & M University
College Station, Texas 77843

I. Introduction

Taal Volcano, which is located in Lake Taal, Batangas, Luzon Island, Philippines, has experienced many past volcanic eruptions, some as early as 1472 [1-3]. The most recent eruption was January, 1968, and lasted from January 31 to March 31.

On September 28, 1965, Taal Volcano erupted [4,5]. One week later, while the Volcano was still in its last stages of solfataric activities, volcanic ash and water samples were collected from localities showing effects of successive volcanic blasts. This study is to determine if the geochemical analyzer of the trace elements, combined with geological and geophysical evidences, may shed some light on the course of events leading to the 1965 eruption.

The following assumptions have been made in this paper:

1. The ash layers represent the early different phases of the 1965 Taal volcanic activity, that is, the first layer representing the initial explosion; the second, the third, and the fourth layers comprise the middle explosion phase, and the final eruption is represented in the fifth layer.
2. The volcanic ash layers were derived from the mixture of juvenile materials and old rocks and were deposited by volcanic steam blasts on the trunk of a tree.
3. The volcanic bomb and olivine-bearing basalt that were taken from the cinder cone are fresh and new materials.
4. The water taken inside the cinder cone was not significantly contaminated by Taal Lake waters.[2]

II. Experimental

A. Field Sampling

Volcanic ash materials were collected from a standing tree trunk in Barrio Alas-as. All that was left of the tree was its trunk and a few broken branches without leaves. The source direction of the successive blasts from the explosion crater were reflected in the apices of the tree-deposited volcanic ashes. (See Fig. 1.) Ash samples were collected from five distinct directional apices. The apices are designated as layers, the first layer being that adjacent to the bark of the tree.

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[1] NAS-IAEA Fellow, the Philippine Atomic Energy Commission.

[2] The cinder cone was breached on October 10, 1965, forming a horseshoe-shape cinder cone.

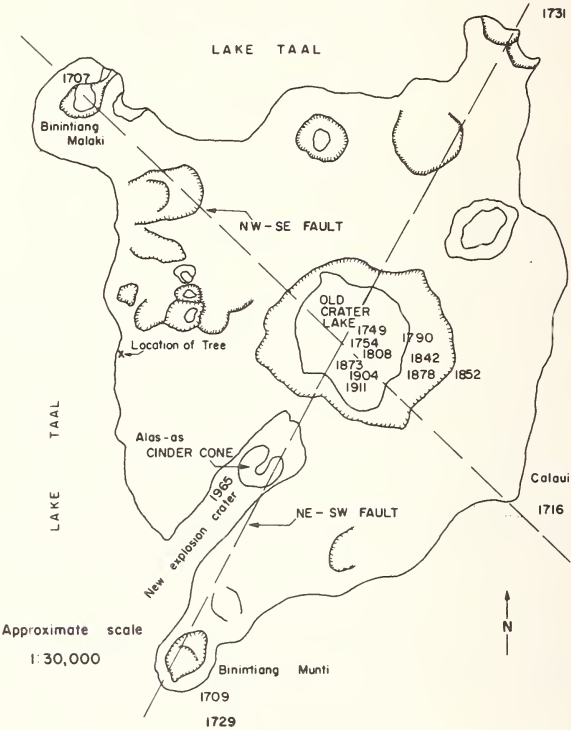

Figure 1. Volcano Island showing the sites of past eruptions and the new (1965) explosion crater.

A volcanic bomb and fragments of olivine-bearing basaltic rock were collected from the cinder cone. The temperatures of the water inside the cinder and old crater lakes were 75 °C and 43.4 °C, respectively, when they were sampled on October 7, 1965. Water samples were also taken from the bubbling waters outside the cinder cone.

B. Procedure

The ash samples were oven dried and sieved with an 80-mesh wire screen. The minus 80-mesh fractions of the ashes, small pieces of volcanic bomb and olivine-bearing basalt weighing from 5-10 mg were sealed in separate polyethylene film bags.

A liter of each of the water samples were evaporated to dryness and 5-10 mg portions of their respective residues were heat sealed in polyethylene bags. A one liter rainwater sample residue collected at the Philippine Atomic Research Center site, Quezon city by the Fallout Group of the Health Physics Dept., Philippine Atomic Research Center from October 1-4, 1965 weighing about 10 mg was similarly prepared. The rainwater residue is believed to include materials ejected during the September 28 volcanic eruptions. The samples were irradiated through the pneumatic tube system of the Philippine Research Reactor (PRR-1) at a flux of about $2 \times 10^{12} \mathrm{n \cdot cm^{-2} \cdot sec^{-1}}$ from 10 to 60 minutes.

The radioactivity produced was measured by gamma-ray spectrometry using a TMC 100 channel analyzer in conjunction with a 1.25 in. × 1.25 in. NaI(Tl) well-type detector. The gamma-ray spectrum was observed at different time intervals in order to follow the decay scheme of the radionuclides produced. The peak area of the photopeaks of interest were obtained by Covell's Method [6].

Fast neutron activation analysis techniques were also done on the ash samples. The objective of the fast neutron activation was to measure the amount of silicon, oxygen, magnesium, iron and aluminum present in the samples. The determinations of the above major elements in the ash depend on the following reactions: $^{27}\mathrm{Al(n,p)}^{27}\mathrm{Mg}$; $^{28}\mathrm{Si(n,p)}^{28}\mathrm{Al}$; $^{56}\mathrm{Fe(n,p)}^{56}\mathrm{Mn}$; $^{16}\mathrm{O(n,p)}^{16}\mathrm{N}$; $^{24}\mathrm{Mg(n,p)}^{24}\mathrm{Na}$; $^{31}\mathrm{P}(\mathrm{n},\alpha)^{28}\mathrm{Al}$; $^{27}\mathrm{Al}(\mathrm{n},\gamma)^{28}\mathrm{Al}$; $^{55}\mathrm{Mn}(\mathrm{n},\gamma)^{56}\mathrm{Mn}$ and $^{19}\mathrm{F}(\mathrm{n},\alpha)^{16}\mathrm{N}$.

These interferences can be handled satisfactorily by the method described by Hislop and Wainerdi [7]. Two previously analyzed rocks (Andes andesite and Columbia River basalt), Hislop [7], were included in the analyses to serve as standards. Irradiation was carried out using a 150 kV Cockcroft-Walton accelerator (Texas Nuclear Corporation) with an approximate neutron flux of about $5 \times 10^{8} \mathrm{n \cdot cm^{-2} \cdot sec^{-1}}$. Information about the experimental set-up used is described by Cuypers [7].

Irradiations were performed for 30 seconds and 5 minutes. The delay time (elapsed time before counting) for the 30 second irradiation was 5 seconds and counting was for 30 seconds using a single channel analyzer which is calibrated to store counts greater than 4.5 MeV. This setting would include the 6.13 and 7.12 MeV peaks of $^{16}\mathrm{N}$ produced by fast neutron activation of $^{16}\mathrm{O}$.

The delay times used for the 5 minute irradiation were 10 minutes and 45 minutes. Gamma-ray spectrometry was done using an RIDL 400 channel analyzer coupled with two matched 3 in. × 3 in. NaI(Tl) Harshaw scintillation detectors. Two detectors were employed to provide improved counting efficiency. The output of the multichannel analyzer was recorded by a Moseley X-Y plotter and a paper tape readout. The data from the punched paper tape is transferred to IBM cards. The IBM cards were processed using an IBM 360 computer programmed with

Yule's [9] "HEVESY" program in order to determine the photopeaks present in the spectrum and to compute the peak areas of the identified photopeaks.

III. Results and Discussion

A. RESULTS

The gamma-ray spectra of the thermal neutron irradiated samples of volcanic ash, olivine basalt and the residue of water from the cinder cone are illustrated in Figures 2, 3, and 4.

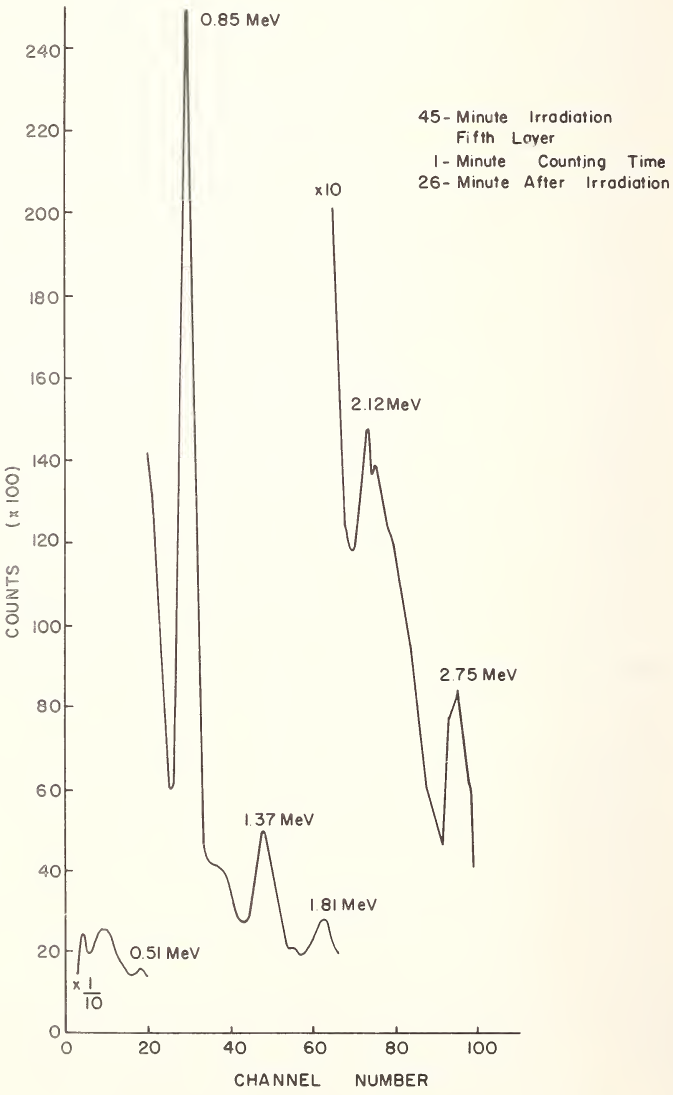

Figure 2. Volcanic ash gamma-ray spectrum.

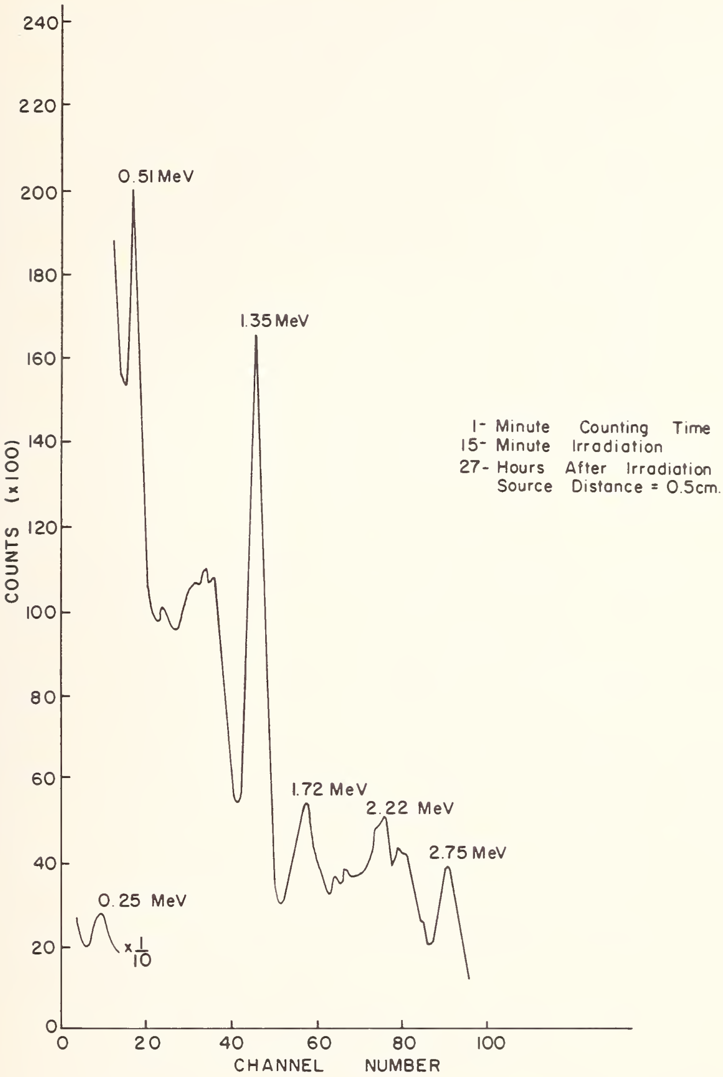

Figure 3. Gamma-ray spectrum of olivine basalt.

Cu, Fe, Na, and Mn are present in all the irradiated samples. Scandium is definitely present in all the ash samples.

The Cu/Na values for the volcanic ash layers, basalt, and volcanic bomb are similar while the Cu/Na values for the water residues may be considered similar except for the Cinder Cone waters which differ by at least a factor of 4. (Table 1)

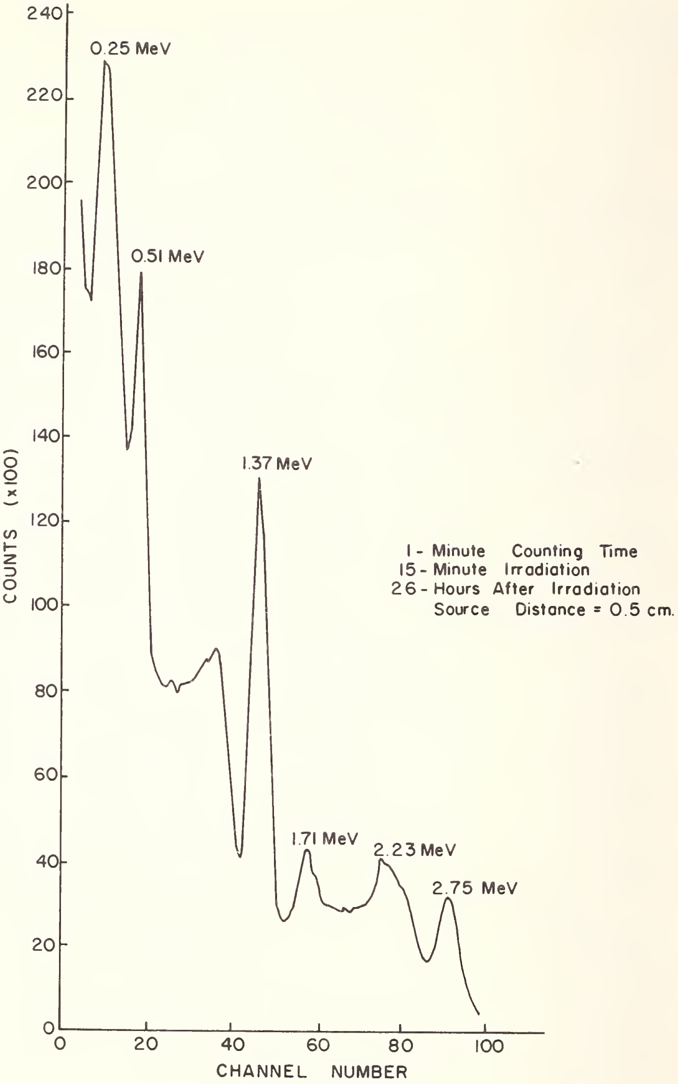

Figure 4. Gamma-ray spectrum of residue of water from cinder cone.

Trace amounts of Ni are present in all the samples. A typical gamma-ray spectrum of the volcanic ash sample produced as a result of fast neutron activation is shown in Figure 5.

Table 2 shows the percentage compositions of Si, Al, Fe, Mg and O of the different volcanic ashes as obtained by 14 MeV neutron activation analysis.

Table 1. Thermal neutron activation analysis results of Taal volcanic products.

Volcanic sample	Approximate computed Cu/Na ratio
Residue of Old Crater Lake Water	.423
Residue of Cinder Cone	2.010
Residue of Bubbling Waters	.291
Residue of PARC Rainwater	.253
Volcanic Bomb	.171
Olivine Basalt from Cinder Cone	.172
Volcanic Ash Layer 1	.184
Volcanic Ash Layer 2	.200
Volcanic Ash Layer 3	.192
Volcanic Ash Layer 4	.178
Volcanic Ash Layer 5	.176

Table 2. Results of fast neutron activation analysis of Taal volcanic products.

Volcanic ash	Aluminum (%)	Iron (%)	Magnesium (%)	Silicon (%)	Oxygen[a] (%)
Layer 2	7.61	5.44	3.60	22.90	45.33
Layer 3	7.98	5.34	3.00	24.40	46.11
Layer 4[b]	7.47	5.47	3.47	21.00	46.94
Layer 5	7.73	6.22	3.50	24.00	50.22

[a] The values for Layer 4 were obtained from duplicate analyses.

[b] The oxygen results were obtained from five separate irradiations of each ash sample.

B. DISCUSSION

The supposition that the volcanic bomb and basalt rocks are juvenile volcanic products makes it appear, based on Table 1, that the ash layers were probably also new pulverized magmatic materials from depth. Assuming that, prior to the magmatic gas blast contamination, the Cu/Na value was fixed for the volcanic ash layers, the results of these analyses indicate that the Cu/Na ratio did not vary from the start of the eruption to the final stages of volcanic activity. The similarity of the Cu/Na values for the volcanic ash layers is shown in Table 1. Thus, it may be suggested that the Cu/Na ratio of the volcanic emanation has remained unchanged throughout the volcanic eruptions.

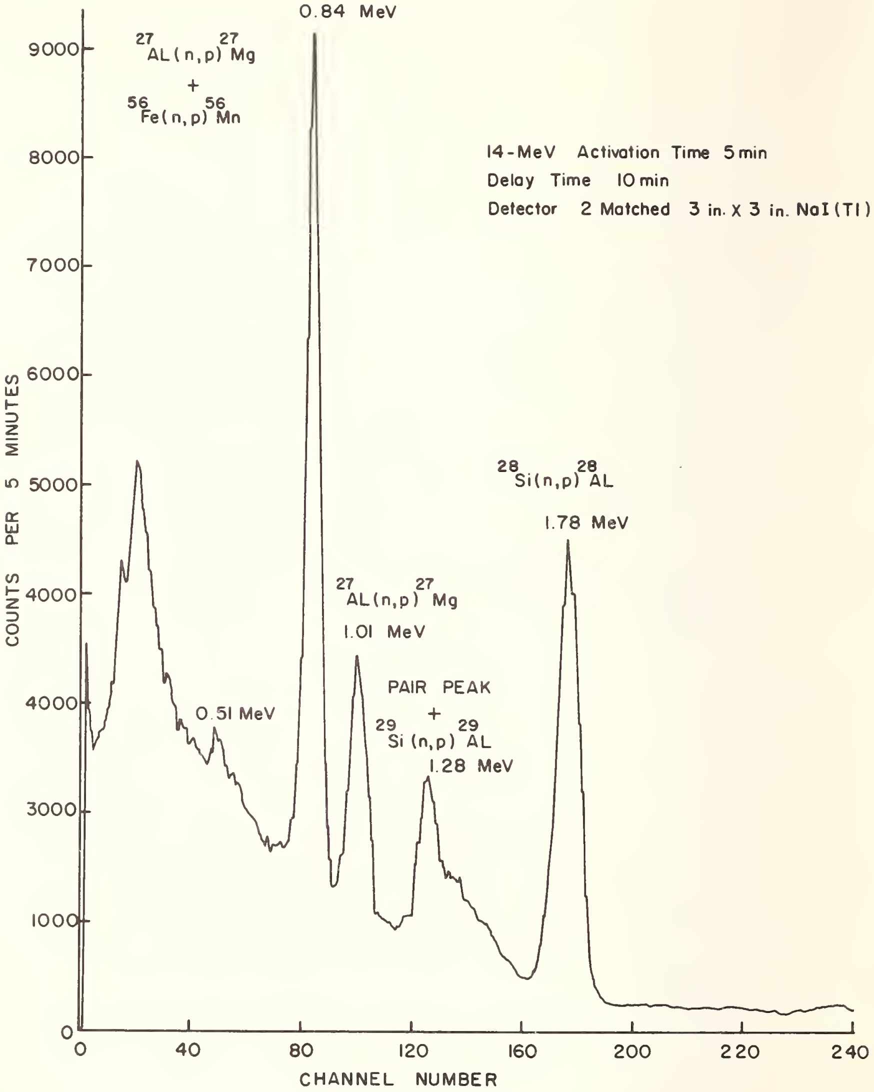

Figure 5. Typical gamma-ray spectrum of the volcanic ash sample emitted after irradiation with fast neutrons.

The Cu/Na ratio was used frequently as a base throughout this study because the ratio involves two important elements that were present in the Taal volcanic emanations, and also because their product radionuclides have prominent characteristic gamma rays, 0.51 MeV (Cu), 1.37 MeV (Na).

The similarity of the Cu/Na ratios for the basalt, volcanic bomb, and volcanic ash samples seem to agree with the position that the recent Taal eruption was not essentially a phreatic eruption [1,4], but that heated ground water or lake water in part was probably mixed with magmatic material. These observations seem to be further substantiated by the latest (January, 1968) Taal eruptions in which lava flows were observed for the first time in recorded history.

IV. Acknowledgment

The authors appreciated the hospitality and fine cooperation extended the senior author during his brief stay in the Taal Volcanic area, by Mr. Arturo Alcaraz, Chief Volcanologist, Commission on Volcanology, Republic of the Philippines, and his staff, specially Messrs. Rogelio Datuin, P. Almoragie, and Alfredo Truncales. The writers also wish to express their appreciation to Chairman E. Vera of Commission on Volcanology for encouraging this fine cooperation between government agencies. To Drs. H. P. Yule and L. E. Fite of the Activation Analysis Research Laboratory we would like to extend our thanks for their valuable assistance and cooperation during the compositional measurement of these samples.

V. References

[1] Alcaraz, A., in Symposium of the 1965 Eruption of Taal Volcano, Manila, 1965.
[2] Bacon, R. F., Phil. Jour. Sci. **1**, 433 (1906).
[3] Bacon, R. F., Phil. Jour. Sci. **2**, 115 (1907).
[4] Moore, J. G., Nakamura, K., and Alcaraz, A., Science **151, 955 (1966).**
[5] Moxham, R. M., Bull. Volcan. **31**, 215 (1967).
[6] Covell, D. F., Anal. Chem. **31**, 1785 (1959).
[7] Hislop, J. S., and Wainerdi, R. E., Anal. Chem. **39**, 29 (1967).
[8] Cuypers, M., and Cuypers, J., Gamma-Ray Spectra and Sensitivities for 14-MeV Neutron Activation Analysis. Texas A & M University, College Station, Texas, 1966.
[9] Yule, H. P., Personal Communication (1968).

ALUMINUM AND SILICON ABUNDANCES OF SOME ITALIAN METEORITES AS DETERMINED BY INSTRUMENTAL ACTIVATION ANALYSIS

Sandro Meloni, Vera Maxia and Silvano Buzzi

Laboratorio di Radiochimica
Istituto di Chimica Generale
Universita di Pavia
27100 Pavia, Italy

I. Introduction

Aluminum and silicon are two major components of chondrites. Several methods for their determination are given in the literature [1] ranging from the classical gravimetric and titrimetric methods to the more recent partially instrumental methods. All these techniques are time consuming and subject to a number of errors.

More recently, silicon and aluminum determination in rocks and meteorites by neutron activation analysis has been proposed by many authors [2-12]. Silicon is determined by irradiation with 14 MeV neutrons through the reaction $^{28}Si(n,p)^{28}Al$ and aluminum by irradiation with thermal neutrons through the reaction $^{27}Al(n,\gamma)^{28}Al$. The results obtained by neutron activation are quite precise and accurate, and the analyses may be performed in a short time. Furthermore, using instrumental neutron activation, the peculiar advantage is obtained of allowing the meteorite samples to be available for further investigations. In this work aluminum and silicon have been determined in eight Italian meteorites by using pile neutrons and irradiating the meteorite samples in two different positions of the Triga Mark II LENA reactor of the University of Pavia.

II. Experimental

A. Meteorites, Standard Rock and Standards

The meteorites and the standard rock analyzed are the following [13,14]: Alfianello, Assisi, Collescipoli, Girgenti, Motta di Conti, Trenzano, Vigarano, Albareto, CAAS Syenite. The first seven meteorites have been supplied by the Milan City Museum of Natural History [15], the eighth meteorite and the standard rock by the Institute of Mineralogy of the University of Modena (Italy) [16].

Three samples for each meteorite have been prepared by grinding to a fine powder the meteorite fragments and weighing 130 to 180 mg aliquots into polyethylene irradiation containers. Two samples of the standard rock already supplied in powder form were put in similar containers. High purity aluminum (99.99%) and semiconductor grade silicon have been used as standards.

B. IRRADIATION

Two series of irradiations have been carried out. The first, aimed at the aluminum analysis took place at the end of the thermalizing column of the 250 kW Triga Mark II pulsing reactor. A thermal flux of about $1.0 \times 10^{9} \text{n}\cdot\text{cm}^{-2}\cdot\text{sec}^{-1}$ and a cadmium ratio for gold greater than 100 were available in this position. Thermal activation only could take place through the reaction $^{27}\text{Al}(\text{n},\gamma)^{28}\text{Al}$. No meaningful interfering fast neutron induced reactions, such as $^{28}\text{Si}(\text{n,p})^{28}\text{Al}$, were observed. The irradiation time was 3 minutes. At the end of the irradiation the samples and the standard were transferred in about 50 seconds to the radiochemistry laboratory 100 meters away by a pneumatic system, and counted.

The second series of irradiations was performed for silicon analysis. It was carried out in a high speed pneumatic system which brought the samples in and out the F-ring of the reactor core in about 3 seconds. Here a thermal flux of about $1.2 \times 10^{12} \text{n}\cdot\text{cm}^{-2}\cdot\text{sec}^{-1}$ and a fast flux (neutron energy greater than 10 keV) of about $1.0 \times 10^{12} \text{n}\cdot\text{cm}^{-2}\cdot\text{sec}^{-1}$ were available. In this position both the thermal and fast neutron induced reactions may occur, in our case the reactions $^{27}\text{Al}(\text{n},\gamma)^{28}\text{Al}$ and $^{28}\text{Si}(\text{n,p})^{28}\text{Al}$. These reactions yield the same product and interfere. This difficulty was overcome by subtracting the contribution due to thermal activation of aluminum, previously determined from the total ^{28}Al activity of the meteorite sample. This correction is made possibly irradiating the meteorite samples together with silicon and aluminum standards. The irradiation time was 3 seconds. At the end of the irradiation the samples were sent to the radiochemistry laboratory for counting as mentioned.

C. RADIOACTIVITY MEASUREMENTS

Activity measurements were carried out by gamma spectrometry with a 7.6 cm × 7.6 cm NaI(Tl) crystal connected to a 400 channel pulse-height analyzer. The 1.78 MeV gamma-ray photopeak from ^{28}Al decay was considered. Five gamma spectra of each meteorite sample and standards were taken successively.

As foreseen, preliminary tests had shown the presence of manganese [17] in meteorites. The 1.81 MeV gamma ray emitted in the ^{56}Mn decay overlaps the 1.78 MeV gamma photopeak from ^{28}Al. The contribution due to ^{56}Mn was evaluated by counting the meteorite samples 45 minutes after the end of irradiation when ^{28}Al had decayed out. This contribution ranged from 3-5% for the first countings to 15-20% for the last ones. Data computation was performed with the aid of an Olivetti desk computer using programs worked out for this purpose.

III. Results and Discussion

A. RESULTS

The aluminum content was evaluated by comparing the net photopeak area for the meteorite sample with the one for the aluminum standard. In Table 1 the percent aluminum in the meteorites is reported together with the existing data in the literature.

The silicon content was evaluated by comparing the photopeak area of the silicon standard with the one for the meteorite after the contribution of aluminum was subtracted. In Table 2 the silicon percent of the meteorites is reported together with the existing data in the literature.

B. DISCUSSION

The validity of the method used and the reliability of the results obtained have been checked by determining silicon and aluminum in the CAAS Syenite. The determined aluminum and silicon contents are in good agreement with the recommended values [29]. An excellent agreement was also obtained with the silicon abundance reported by Vincent [6], who performed the analysis through activation with 14 MeV neutrons.

Of all the possible interfering reactions, the contribution due to the reaction ^{31}P(n,α)^{28}Al was considered negligible on account of its low cross section.

Precision is about 3-4% in the aluminum analysis and 2-3% in the silicon analysis, the latter being somewhat higher because of the improved counting statistics due to the higher flux available. Accuracy, which was evaluated by taking into account every possible source of error, may be considered to be about 5-6%.

Comparison of the results of this work with all the existing values in the literature is not very significant. Most of the previous analyses are very old and the results questionable, especially for aluminum. Comparison is thereafter confined to the more recent analyses. A certain discrepancy may be seen for the aluminum abundance: our results for Alfianello are in an acceptable agreement with those obtained by Fisher [4] using neutron activation.

A better agreement is obtained in the silicon analysis, especially for Albareto and Vigarano. A peculiar feature of the silicon abundances

Table 1. Aluminum content of the eight Italian meteorites analyzed.

Meteorite	Aluminum content found %	Previous data (Al%)	
ALB – 1	1.30	2.37	Maissen 1880 [18]
ALB – 2	1.20	1.70	Gallitelli 1939 [19]
ALB – 3	1.37		
Mean value	1.29 ± 0.05		
ALF – 1	1.24	0.94	Maissen 1884 [20]
ALF – 2	1.40	0.47	Foullon 1883 [21]
ALF – 3	1.22	1.38	Fisher 1964 [14]
Mean value	1.28 ± 0.06		
ASS – 1	1.25		
ASS – 2	1.30		
ASS – 3	1.26		
Mean value	1.27 ± 0.02		
COL – 1	1.24	0.49	Trottarelli 1890 [22]
COL – 2	1.18	3.40	Merril 1916 [23]
COL – 3	1.16	1.94	Wiik 1956 [24]
Mean value	1.19 ± 0.02		
GIR – 1	1.27	0.76	Rath 1869 [25]
GIR – 2	1.09		
GIR – 3	1.34		
Mean value	1.23 ± 0.07		
MDC – 1	1.09	0.56	Denza 1868 [26]
MDC – 2	0.99		
MDC – 3	0.95		
Mean value	1.01 ± 0.04		
TRE – 1	1.14	1.59	Curioni 1858 [27]
TRE – 2	1.11		
TRE – 3	1.18		
Mean value	1.14 ± 0.02		
VIG – 1	1.87	1.75	Mason 1963 [28]
VIG – 2	2.09		
VIG – 3	2.03		
Mean value	2.00 ± 0.07		
SYENITE – 1	4.88	4.92	Value recommended by Webber 1965 [29]
SYENITE – 2	5.00		
Mean value	4.94 ± 0.1		

obtained by Vogt [5] through fast neutron activation analysis is that the Si percent is always lower than ours. A similar observation was also made by Mason [17] for the olivine-hyperstene chondrites analyzed by Vogt.

Summarizing the aluminum and silicon abundances of the meteorites analyzed in this work according to their classification [13,14], a

Table 2. Silicon content of the eight Italian meteorites analyzed.

Meteorite	Silicon content found %	Previous data (Si %)	
ALB – 1	19.0	16.77	Maissen 1880 [18]
ALB – 2	18.7	18.86	Gallitelli 1939 [19]
ALB – 3	18.0		
Mean value	18.6 ± 0.3		
ALF – 1	17.9	17.56	Maissen 1884 [20]
ALF – 2	18.9	17.6	Vogt 1965 [5]
ALF – 3	18.1	18.3	
Mean value	18.3 ± 0.3		
ASS – 1	17.5		
ASS – 2	16.4		
ASS – 3	16.1		
Mean value	16.7 ± 0.4		
COL – 1	19.4	14.50	Trattorelli 1890 [22]
COL – 2	17.3	16.15	Merril 1916 [23]
COL – 3	18.4	16.91	Wiik 1956 [24]
Mean value	18.4 ± 0.6	17.5	Vogt 1965 [5]
GIR – 1	19.9	16.96	Rath 1869 [25]
GIR – 2	19.0		
GIR – 3	19.5		
Mean value	19.5 ± 0.3		
MDC – 1	16.8	18.50	Denza 1868 [26]
MDC – 2	16.4		
MDC – 3	16.1		
Mean value	16.4 ± 0.2		
TRE – 1	17.5	19.52	Curioni 1858 [27]
TRE – 2	16.3	15.6	Vogt 1965 [5]
TRE – 3	18.7		
Mean value	17.5 ± 0.7		
VIG – 1	15.7	15.37	Mason 1963 [28]
VIG – 2	15.1	15.35	Wing 1964 [2]
VIG – 3	15.4		
Mean value	15.4 ± 0.2		
SYENITE – 1	27.7	27.79	Value recommended by Webber 1965 [29]
SYENITE – 2	27.8		
Mean value	27.75 ± 0.05	27.77	Vincent 1967 [6]

comparison can be made with the recommended values for each class [17]. In Table 3 the average values for each class and the values reported by Mason [17] are given. It can be seen that within the experimental errors quite a good agreement is obtained.

Table 3. Average abundance of aluminum and silicon in the various classes of chondrites.

Class	Meteorite	Al percent this work	Al percent recommended value	Si percent this work	Si percent recommended value
Olivine – Hyperstene	Albareto	1.29		18.6	
	Alfianello	1.28		18.3	
	Girgenti	1.23		19.5	
	Mean value	1.27	1.27	18.8	18.7
Olivine – Bronzite	Assisi	1.27		16.7	
	Collescipoli	1.19		18.4	
	Motta di Conti	1.01		16.4	
	Trenzano	1.14		17.5	
	Mean value	1.15	1.22	17.2	17.1

IV. References

[1] Smales, A. A., and Wager, L. R., Ed., Methods in Geochemistry, Interscience Publ. Ltd., London, 1960, pp. 33-80.
[2] Wing, J., Anal. Chem. **36,** 559 (1964).
[3] Fisher, D. E., Meteoritics **2,** 137 (1964).
[4] Fisher, D. E., Geochim. Cosmochim. Acta **28,** 743 (1964).
[5] Vogt, J. R., and Ehmann, W. D., Geochim. Cosmochim. Acta **29,** 373 (1965).
[6] Vincent, H. A., and Volborth, A., Nucl. Appl. **3,** 753 (1967).
[7] Hofler, H., and Sorantin, H., unpublished data.
[8] Ehmann, W. D., and Durbin, D. R., Geochim. Cosmochim. Acta **32,** 461 (1968).
[9] Smales, A. A., Lab. Pract. **16,** 701 (1967).
[10] Schmitt, R. A., and Smith, R. H., General Atomic Report, GA-5900 (1964).
[11] Schmitt, R. A., and Smith, R. H., General Atomic Report, GA-6414 (1965).
[12] Schmitt, R. A., and Smith, R. H., General Atomic Report, GA-7424 (1966).
[13] Baldanza, B., Min. Mag. **35,** 214 (1965).
[14] Hey, M. H., Catalogue of Meteorites, III Ed., The British Museum London, 1966.
[15] De Michele, V., Atti Soc. It. Sci. Nat. Milano **104,** 225 (1965).
[16] Levi Donati, G., Atti Accad. Naz. Sci. Lett. Arti, Modena **18,** 1 (1960).
[17] Mason, B., Am. Museum Novitates No. 2223 (1965).
[18] Maissen, P., Gazz. Chim. Ital. **10,** 20 (1880).
[19] Gallitelli, P., Period. Min., Roma **10,** 345 (1939).
[20] Maissen, P., Gazz. Chim. Ital. **13,** 369 (1884).
[21] Foullon, H., S. B. Akad. Wiss, Wien **88,** 433 (1883).
[22] Trotterelli, G., Gazz. Chim. Ital. **20,** 611 (1890).

[23] Merril, G. P., Mem. Nat. Acad. Sci., Washington **14,** 13 (1916).
[24] Wiik, H. B., Geochim. Cosmochim. Acta **9,** 279 (1956).
[25] Rath, G., Ann. Phys. Chem. Poggendorf **138,** 541 (1869).
[26] Denza, F., Nuovo Cimento **28,** 145 (1868).
[27] Curioni, M. E., Atti R. Ist. Lomb. Sci. Milano **1,** 457 (1858).
[28] Mason, B., Space Sci. Rev. **1,** 621 (1963).
[29] Webber, G. R., Geochim. Cosmochim. Acta **29,** 229 (1965).

NEUTRON ACTIVATION ANALYSIS OF INDIVIDUAL COSMIC SPHERULES[1]

H. T. Millard, Jr.

U.S. Geological Survey
Denver, Colorado 80225

I. Introduction

Microscopic objects called "cosmic" spherules are found in highest concentration in deep oceanic sediments where the rates of sedimentation are extremely slow. Since the discovery of cosmic spherules a century ago, it has been assumed that they were spalled off the molten surfaces of iron meteorites during the violent flight of these bodies through the atmosphere. The evidence for this conclusion lies in the presence of Fe-Ni cores within the spherules and the occurrence of spherules at the locations of iron meteorite falls. Other origins that have been proposed are cosmic dust (*i.e.*, rather than being removed from the surfaces of meteorites, they may arrive at the earth as dust), volcanism, and industrial contamination (*e.g.*, welding spherules). The extraterrestrial origins of the individual particles in any collection of cosmic spherules are suspect owing to the likelihood of contamination from terrestrial sources. Thus it is important to establish criteria which differentiate extraterrestrial materials from terrestrial contaminants.

Three methods that are available for the identification of extraterrestrial material are: (1) observation of fall (*e.g.*, meteorites); (2) comparison of chemical and mineralogical composition to the composition of material seen to fall; or (3) detection of nuclides produced by cosmic-ray bombardment. For extremely small extraterrestrial particles, such as cosmic spherules, only the third method is truly unambiguous. However, the second method may be valid if the concentrations of the chemical elements measured differ markedly from those expected in terrestrial contaminants.

Analytical techniques that have been applied to cosmic spherules include neutron activation analysis to measure cobalt, nickel, and copper in aggregate spherule samples [1], instrumental neutron activation analysis to measure iron in individual spherules [2], and use of the electron microprobe to measure iron, nickel, cobalt, and manganese in individual spherules [3-5]. Instrumental neutron activation analysis (INAA) was chosen for this study because it is nondestructive and has sufficient sensitivity to measure elemental concentrations in individual 50 to 100 microgram particles. A 1-1/2 ton sample of Pacific Ocean sediment was processed to isolate the cosmic spherules. From this sample, 150 to 350 micron diameter spherules were chosen for study.

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[1] Publication authorized by the Director, U.S. Geological Survey.

II. Experimental

A. APPARATUS

All counting was done with a gamma spectrometer consisting of an unshielded 20 cm^3 Ge(Li) detector coupled to a 1024 channel analyzer. The resolution of the system was 4.5 keV full width at half maximum (FWHM) for the ^{60}Co 1.17 MeV photopeak. Peak heights were read from the plotted spectra using the 368, 1114, and 1482 keV photopeaks of ^{65}Ni; the 847 and 1811 keV photopeaks of ^{56}Mn; the 1098 and 1289 keV photopeaks of ^{59}Fe; the 296, 308, 318, and 468 keV photopeaks of ^{192}Ir; and the 1173 and 1332 keV photopeaks of ^{60}Co.

B. PROCEDURE

For the measurement of the short-lived nuclides, 2.56 h ^{65}Ni and the 2.58 h ^{56}Mn, as well as 45 day ^{59}Fe, the spherules were mounted on mica sheets for irradiation. This type of mounting was used in order to record fission tracks from the uranium in the spherules. NiO and Mn_3O_4 spectrographic-grade powders were used as flux monitors. The samples were irradiated for 6 hours in a glory tube in the Naval Research Reactor where the neutron flux was about 5×10^{12} $n \cdot cm^{-2} \cdot sec^{-1}$. Following irradiation, the spherules were removed from the mica sheets and were gamma counted within several hours.

For the measurement of the long-lived nuclides, 74 day ^{192}Ir, 45 day ^{59}Fe, and 5.3 year ^{60}Co, the spherules were wrapped in aluminum foil and irradiated, along with monitors consisting of evaporated solutions of iridium, cobalt, and iron, in the Argonne National Laboratory CP-5 reactor for 7 days. An isotope tray position was used in which the neutron flux was about 5×10^{12} $n \cdot cm^{-2} \cdot sec^{-1}$. The radioactivity was allowed to decay for 7 days and then the spherules were gamma counted.

III. Results and Discussion

A. RESULTS

The concentrations of nickel, cobalt, manganese, and iridium measured in the spherules are shown in Table 1. These data have been normalized to the concentration of iron in each sample in order to reconstruct the unoxidized composition of the spherules and, thereby, facilitate comparison to the literature data for iron meteorites and terrestrial materials. When the manganese content is high, only an upper limit to the nickel content can be measured. When the manganese content is very low, only an upper limit to the manganese concentration can be established because of the interfering reaction, $^{56}Fe(n,p)^{56}Mn$. Iridium can be measured with extreme sensitivity as shown by the upper limit for the welding spherule which represents only 4 picograms iridium. Specific gravities are also shown for a number of spherules.

B. Discussion

During separation from the sediment, the spherules were sorted into morphologically distinct groups with surface roughness increasing from Type A through Type C (Table 1). Type D particles are subrounded.

Table 1. Bulk compositions of spherules measured by instrumental neutron activation analysis.

Spherule		Specific gravity	Ni/Fe	Co/Fe ($\times 10^6$)	Mn/Fe ($\times 10^6$)	Ir/Fe ($\times 10^6$)
Type A:	A2	6.7	0.12	4,000	<20	8
	A3	5.7	0.06	5,000	<20	0.5
	A6	4.9	0.03	4,000	< 9	3
	A8	4.7	0.13	4,000	<20	7
	A9	4.8	0.08	3,000	<18	3
Type B:	B15	5.8	0.06	4,000	< 5	0.6
	B4	2.8	<0.9	3,000	8,000	–
	B13	2.6	<0.1	2,000	7,000	–
Type C:	C3	5.7	<0.2	9,000	< 3	–
	C6	2.5	<0.3	1,000	1,000	–
Type D:	D13	–	<0.7	2,000	6,000	–
Welding spherule		7.7	<0.06	50	500	<0.02
Iron meteorites		7.8	0.04–0.4	5,000–10,000	1	0.3–15
Volcanic magnetites		–	–	–	5,000–30,000	–
Mafic rocks (average)		–	0.002	500	20,000	–

Presumably the conventional cosmic spherules are represented by Type A with the ratio of cosmic spherules/terrestrial contamination decreasing through Types B and C. No cosmic spherules were expected in the Type D material.

The Ni/Fe and Co/Fe ratios do not vary by more than a factor of 10 among the spherules listed in Table 1. On the other hand, the Mn/Fe ratios vary by a factor of at least 1000. Iridium was not measured in all the spherules listed, but in those in which it was determined its concentration is about 1000 times the concentration expected in terrestrial materials. Thus, the spherules may be divided into two groups: (1) low manganese, high iridium, and high specific gravity (all Type A spherules and spherules B15 and C3), and (2) high manganese, probably low iridium, and low specific gravity spherules B4, B13, C6 and D13). The spherules in the first group must come from iron meteorites whereas those in the second group are probably terrestrial. More data on the Mn/Fe and Ir/Fe ratios in terrestrial materials are needed before the sources of the terrestrial particles can be established with certainty.

IV. References

[1] Smales, A. A., Mapper, D., and Wool, A. J., Geochim. et Cosmochim. Acta **13,** 123 (1968).

[2] Cassidy, W. A., in Cosmic Dust, H. E. Whipple, Ed., New York Acad. Sci. Ann. **119,** Art. 1, pp. 318-338 (1964).

[3] Castaing, R., and Fredriksson, K., Geochim. et Cosmochim. Acta **14,** 114 (1958).

[4] Schmidt, R. A., and Keil, K., Geochim. et Cosmochim. Acta **30,** 471 (1966).

[5] Hodge, P. W., and Wright, F. W., in Symposium on Meteor Orbits and Dust, Smithsonian Astrophys. Obs. **11,** 381 (1967).

EXTENSIONS OF THE USE OF Ge(Li) DETECTORS IN INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS OF GEOLOGICAL SAMPLES[1]

G. E. Gordon, J. C. Dran, P. A. Baedecker[2]
and C. F. L. Anderson[3]

Department of Chemistry and Laboratory for Nuclear Science
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

I. Introduction

Recently Gordon *et al* [1] showed that the concentrations of more than 20 elements in standard rocks can be determined by neutron activation followed by the taking of gamma-ray spectra with a Ge(Li) detector several times after irradiation. We have extended the use of Ge(Li) detectors in instrumental neutron activation analysis (INAA) to very short-lived species and to classes of geological samples not considered in the previous study.

Samples and monitors were irradiated for 30 to 60 sec at a thermal-neutron flux of $2 \times 10^{13} \mathrm{n \cdot cm^{-2} \cdot sec^{-1}}$ in the MIT reactor. Samples were delivered to the laboratory within 6 sec after the end of irradiation *via* a pneumatic tube system. Within 3 min after irradiation we started taking gamma-ray spectra of the sample and monitor with a 30 $\mathrm{cm^3}$ Ge(Li) detector and 4096 channel analyzer. The full width at half-maximum (FWHM) of the photopeak produced by 662 keV gamma rays was about 7 keV. Spectra stored in the analyzer memory could be recorded within a few seconds on magnetic tape, allowing us to take spectra in rapid succession.

The spectra of neutron irradiated rocks taken within a few minutes after irradiation are in general dominated by 2.3 min ^{28}Al. However, Al abundances are sufficiently small in ultramafic rocks and stony meteorites that one can also observe gamma rays from 3.8 min ^{52}V and 9.5 min ^{27}Mg as shown in Figure 1. Concentrations of the three elements can be determined by comparison of the photopeak areas with those of the

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[2] Present address: Department of Chemistry, U.C.L.A., Los Angeles, California.

[3] Present address: Department of Chemistry, Stanford University, Palo Alto, California.

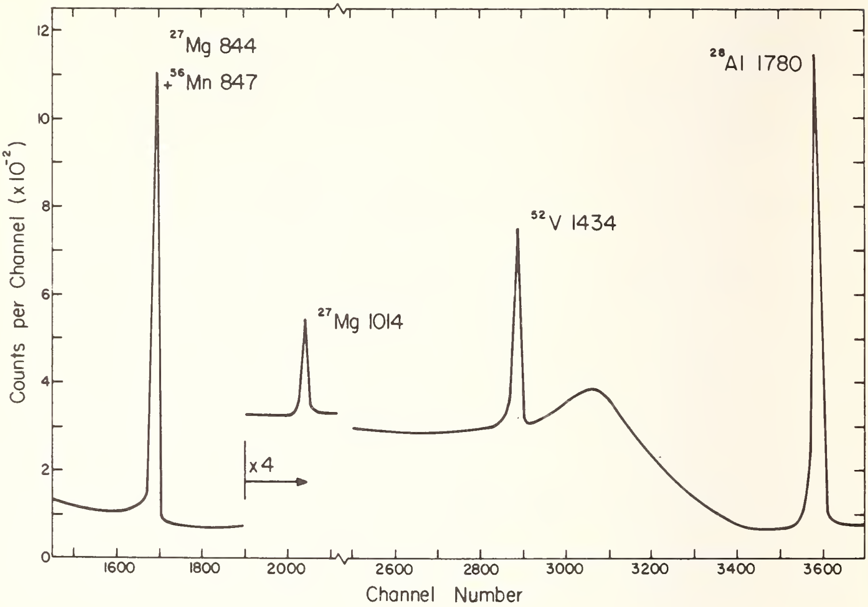

Figure 1. Gamma-ray spectrum of neutron activated meteorite sample observed with a 30 cm^3 Ge(Li) within a few minutes after irradiation. (Numbers attached to peaks are energies in keV.)

corresponding peaks in the spectrum of the monitor solution. For ^{27}Mg it was necessary to use the peak at 1014 keV, since the one at 844 keV contains a large contribution from the 847 keV line of 2.6 h ^{56}Mn.

As examples of determination of the concentrations of these elements, we list preliminary results for two USGS standard rocks and several meteorites in Table 1. We have also listed literature values for these abundances, if available. Agreement between this and previous studies is generally good.

Accuracy of the determinations involving the short-lived species is not high (±several percent in most cases). Major sources of error are poor statistics and timing errors. Statistics are limited by the fact that samples cannot be counted for more than about 5 min initially, since one must count both the sample and monitor before the short-lived species are gone. Timing errors are important because the total counting rate of the samples changes substantially during the counts. Not only does one have to make a first order correction for decay of the activity in question over the true duration of the count, but often there is an appreciable second order correction [2] for the change of dead time fraction during the count. Now that we know that the early spectra are relatively uncomplicated, we could reduce both sources of error by using lower amplifier gain. This would shift the spectrum down to lower channel numbers, thereby reducing the average dead time per pulse.

Table 1. Concentrations of aluminum, magnesium and vanadium in ultramafic rocks and stony meteorites.

	Concentration		
Sample	Aluminum (%)	Magnesium (%)	Vanadium (ppm)
This work:			
PCC–1	0.37	25.5	37
DTS–1	0.13	30.6	6
Chondrites:			
Plainview (H–group)	1.2	12	60
Forest City (H–group)	1.4	10	50
Harleton, Texas (L–group)	1.3	14	85
Bruderheim (L–group)	1.4	15	75
Waltoun, Ky. (L–group)	1.1	12	50
Achondrites:			
Johnstown (Hypersthene)	0.7	11	105
Cumberland Falls	0.1	30	~9
Literature:			
PCC–1[a]	0.37	26.0	20–38
DTS–1[a]	0.15	29.6	9–16
Typical chondrite	0.8 –1.85[b] 1.2 –1.9[d]	10–16[b]	62–77[c]
Typical achondrite[b]	0.13–1.4	15–23	

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[a] Flanagan, F. J., Geochim. Cosmochim. Acta **31**, 289 (1967).

[b] Urey, H. C. and Craig, H., Geochim. Cosmochim. Acta **4**, 36 (1953).

[c] Kemp, D. M. and Smales, A. A., Anal. Chim. Acta **23**, 397 (1960).

[d] See reference [3].

As Fischer [3] has demonstrated, the ^{28}Al activity of neutron irradiated rocks can be measured with NaI detectors. The accuracy of such determinations is likely as high or higher than that obtainable with Ge(Li) detectors. However, the superior resolution of Ge(Li) detectors is likely required to make the ^{27}Mg and ^{52}V photopeaks show up above the large Compton plateaus of higher energy gamma rays.

II. Other Types of Samples

A. MANGANESE NODULES

Recently there has been considerable interest in the composition of Mn nodules, for example, Refs. [4] and [5]. These nodules consist largely of

Fe and Mn oxides and are typically spheroidal objects of weights in the tens to hundreds of grams. They appear to be quite abundant on the sea floor.

Manganese nodules present an interesting problem for INAA: they have very high concentrations of Mn, Fe and Co which generally give considerable interference in INAA determinations of trace element concentrations, but they are very rich in many interesting trace elements. Typical concentrations are: Th 50 parts per million (ppm), La 500 ppm, Ce 2000 ppm, Eu 150 ppm [5]. In order to test our method we irradiated pieces of three nodules and took gamma-ray spectra with the 30 cm^3 detector and an 8 cm^3 detector (FWHM ~3.7 keV at 662 keV) at several times later. We now have only preliminary estimates of the concentrations of the elements observed. However, it is clear that the method can be used to determine concentrations of the following elements: rare earths La, Ce, Sm, Eu, Tb, Yb and Lu; transition elements Sc, Fe, Co and Mn; also Na, Th, Hf and Sb. It will likely be possible to measure the concentrations of Cs, Rb, Cr and Ba in some cases.

B. MICROTEKTITES

In 1967, Glass and Heezen [6] reported finding small (<1 mm diam), glassy spherules in deep sea sediment cores from the Indian Ocean. As these spherules appeared to be related to tektites, they were designated "microtektites". In order to further check the compositions of the spherules and compare them with those of ordinary tektites, five of the spherules were irradiated collectively and their spectra observed with the 30 cm^3 Ge(Li) detector. This project introduces the problem of small sample size as the total sample weight was only 1.5 mg. A 30 min irradiation time was used for short-lived species (2 to 15 h half lives) and an 8 h period for longer-lived activities. Following the former we observed ^{24}Na, ^{65}Mn, ^{42}K, ^{152m}Eu, and ^{165}Dy; from the latter we obtained ^{46}Sc, ^{140}La, ^{141}Ce, ^{153}Sm and ^{233}Pa [from $^{232}Th(n,\gamma)^{233}Th \xrightarrow{\beta} {}^{233}Pa$]. Analysis of the data is still in progress; however, it appears that with the possible exception of Na, the concentrations of the elements determined are in excellent agreement with those of tektites, particularly the indochinities.

III. Conclusions

Except for the short-lived species ^{28}Al and, in meteorites and ultramafic rocks, ^{52}V and ^{27}Mg, we have not been able to observe any species in addition to those found by Gordon, *et al* [1]. We doubt that the concentrations of many additional elements can be determined in geological samples by INAA with simple Ge(Li) detectors. It is likely that the next major advances in the technique will come with the use of Ge(Li) detectors coupled with anti-Compton shields. Also, Ge(Li)-NaI(Tl) coincidence counting may be useful, although reduction of the enormous amount of data will be a problem. However, we have been able to observe most of the species of Ref. [1] in Mn nodules and we have demonstrated the usefulness of the technique for very small samples.

IV. Acknowledgments

We wish to thank Dr. Frank Manheim of Woods Hole Oceanographic Institute for providing the Mn nodule samples and Dr. Billy Glass of Lamont Geological Observatory for the microtektites.

V. References

[1] Gordon, G. E., Randle, K., Goles, G. G., Corliss, J. B., Beeson, M. H., and Oxley, S. S., Geochim. Cosmochim. Acta **32,** 369 (1968).
[2] Low, K., Nucl. Instrum. Meth. **26,** 216 (1963).
[3] Fisher, D. E., Geochim. Cosmochim. Acta **28,** 743 (1963).
[4] Barnes, S. S., Science **157,** 63 (1967).
[5] Ehrlich, A. M., Thesis, Dept. of Chemistry, M.I.T., March 1968, unpublished.
[6] Glass, B. P., and Heezen, B. C., Scientific American **217,** No. 1, 32 (1967).

NEUTRON TECHNIQUES FOR *IN SITU* ELEMENTAL ANALYSIS

John W. Mandler and John H. Reed

IIT Research Institute
10 West 35th Street
Chicago, Illinois 60616

I. Introduction

Techniques for *in situ* compositional analysis have become important in many fields such as geology, oceanology, and space studies. A combined neutron experiment simultaneously employing capture gamma-ray analysis, activation analysis, inelastic neutron scattering, and thermal neutron die-away techniques for remote analysis is presently being developed by NASA[1]. Although this experiment is intended for lunar and planetary surface analysis, terrestrial applications in geology and oceanology are apparent.

The four techniques in the combined experiment are being integrated into a single package and will use the same gamma-ray detector and high energy neutron source. The neutron source selected by NASA is a generator which produces 14 MeV neutrons *via* the $^{3}H(d,n)^{4}He$ reaction. The generator was chosen (instead of an isotopic neutron source) because it can be turned off during the space flight, thus avoiding activation of the equipment carried on the spacecraft. Moreover, a background spectrum can be obtained from the planetary surface before the neutron generator is turned on. A 3 in. × 3 in. NaI(Tl) crystal was selected as the gamma-ray detector instead of a superior resolution solid state detector because of the problems involved in keeping a solid state detector cool during the spaceflight.

For terrestrial applications the neutron source and gamma-ray detector should be chosen on the basis of the needs of the particular application. The use of both types of neutron sources and gamma-ray detectors are considered in this paper.

II. Measurements Using an Isotopic Source

The composite capture, inelastic, and activation gamma-ray spectra from large samples of basalt and granite have been obtained using Pu-Be neutron source and NaI(Tl) and Ge(Li) detectors. To obtain these spectra the source and detector are placed on the surface of the sample. An 8 cm thick polyethylene neutron reflector is placed above the source in order to increase the thermal flux on the surface of the sample. The detector is surrounded by a Li^6F thermal neutron shield and a 6 in. tungsten shadow shield is used between the source and detector to attenuate the fast neutrons from the source and the hydrogen capture gamma rays from the polyethylene.

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[1] This joint effort involving IIT Research Institute (capture gamma ray), Lawrence Radiation Lab (inelastic scattering), Mobil Oil (neutron die-away), and Texas A&M (Activation Analysis) is sponsored and coordinated by the NASA.

Figure 1 shows the gamma-ray spectrum obtained from basalt using a Pu-Be neutron source and a 3 in. × 3 in. NaI(Tl) detector. Capture gamma-ray peaks due to iron, titanium, calcium, silicon, and hydrogen are present together with activation peaks due to oxygen and silicon. Inelastic gamma-ray peaks from oxygen, silicon, and magnesium are also present.

Several of the peaks in Figure 1 are composed of many distinct gamma-ray lines that cannot be resolved using a NaI(Tl) detector. Figure 2 shows a portion of this same gamma-ray spectrum from basalt, however, replacing the NaI(Tl) detector with a 5 cm^3 Ge(Li) detector. With the superior resolution of this detector the iron doublet has been resolved and

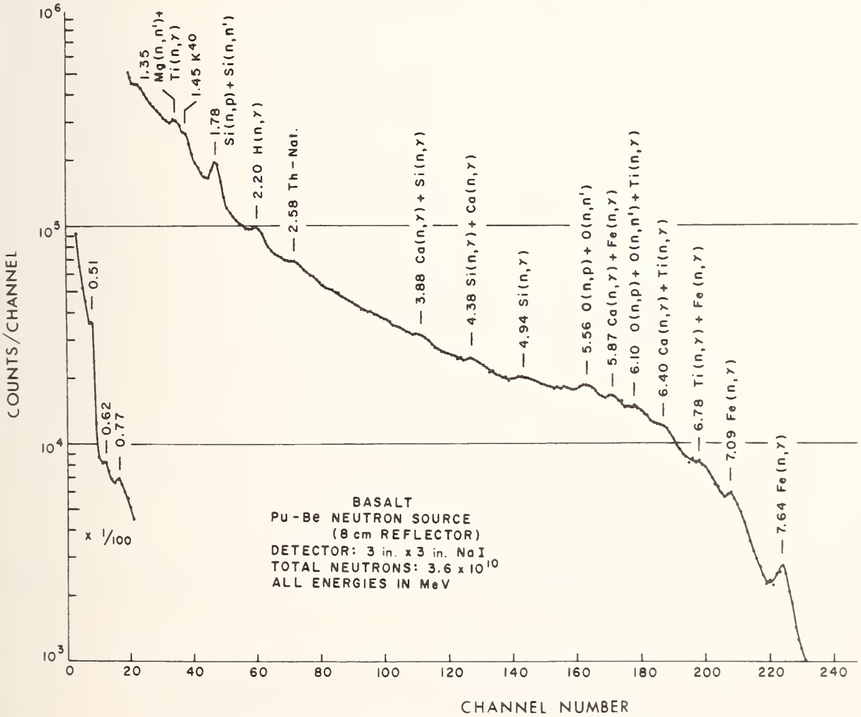

Figure 1. Gamma-ray spectrum from basalt obtained using NaI(Tl) detector and isotopic neutron source.

capture gamma-ray peaks from sodium and manganese (which were not evident in the NaI(Tl) spectrum) are seen. A lower energy portion of the Ge(Li) spectrum (not shown) contained gamma-ray lines from the additional elements, hydrogen and magnesium. Areas of individual peaks which could not readily be obtained from the NaI(Tl) spectrum can be obtained from the Ge(Li) spectrum. The accurate determination of peak areas is a prerequisite for determining the composition of the sample using these neutron techniques. Therefore, the data obtained using an isotopic neutron source contain a far greater amount of useful information when a high resolution solid state detector is used.

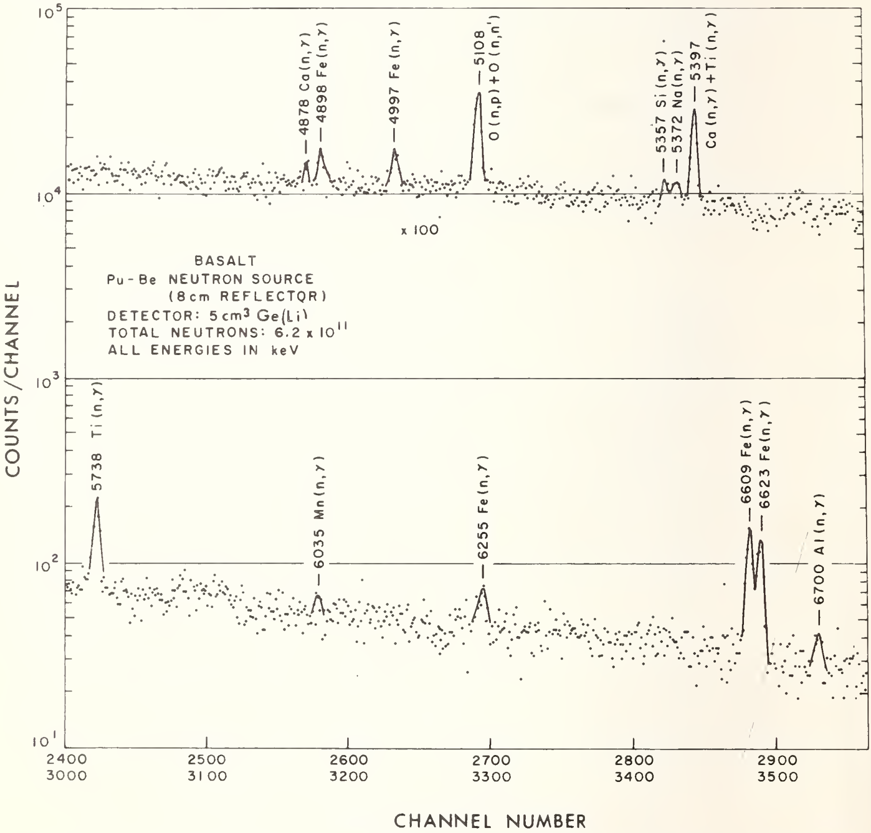

Figure 2. Gamma-ray spectrum from basalt obtained using Ge(Li) detector and isotopic neutron source.

III. Measurements Using a Neutron Generator

Both NaI(Tl) and Ge(Li) detectors have been used to measure the gamma-ray spectra emitted from basalt and granite when irradiated with a pulsed 14 MeV neutron source. The pulsed nature of the source permits the separation of the inelastic, capture, and activation portions of the spectrum. The inelastic gamma rays are prompt (*i.e.*, they are emitted only during the neutron pulse) while the capture gamma rays build up during and immediately after the pulse and then exhibit exponential decay between pulses. The activation gamma rays build up during each pulse and exhibit negligible decay between pulses since their half lives are long compared to the time between pulses. Therefore, by gating the analyzer on during each pulse and off between pulses the pure inelastic spectrum is collected. (The intensity of the capture and activation gamma rays emitted during the pulse is negligible compared to the intensity of the inelastic gamma rays). Sampling for an interval just before each neutron pulse yields the cyclic activation spectrum (since the capture gamma rays have decayed away by this time), and sampling for an interval just after each neutron pulse yields the combined capture plus activation spectrum. Subtraction of the cyclic activation spectrum from the combined spectrum yields the pure capture gamma-ray spectrum.

The combined spectrum from basalt using a NaI(Tl) detector (Figure 3) contains lines identifiable as capture gamma rays from iron, titanium,

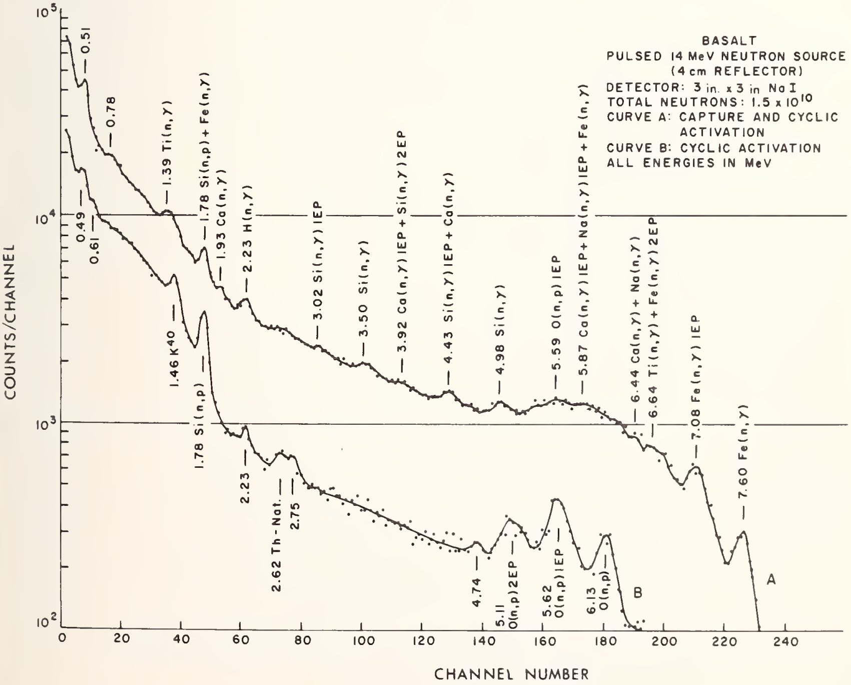

Figure 3. Capture and cyclic activation spectra from basalt obtained using NaI(Tl) detector and pulsed neutron source.

calcium, silicon, and hydrogen and cyclic activation gamma rays from oxygen and silicon. The prompt or inelastic spectrum (not shown) contains lines attributable to sodium, iron, magnesium, aluminum, silicon, and oxygen.

Data has been collected using a Ge(Li) detector in conjunction with a pulsed 14 MeV neutron generator. The combined capture plus activation spectrum is very similar to Figure 2. The major advantage that a Ge(Li) detector has over a NaI(Tl) detector when a pulse neutron generator is used is in the case of the data analysis and the precision of the results.

Thus, if a NaI(Tl) detector must be used, then it is advantageous to use a pulsed neutron generator for timing purposes. However, if a Ge(Li) detector can be used, a pulsed neutron generator offers little advantage over an isotopic source other than the ability to turn the generator on or off at the experimenter's discretion.

SIMULTANEOUS MEASUREMENT OF SEVENTEEN TRACE ELEMENTS IN EIGHT GEOCHEMICAL STANDARDS: A NOVEL ADAPTATION OF NEUTRON ACTIVATION ANALYSIS

D. R. Case, J. C. Laul, M. A. Wechter,
F. Schmidt-Bleek and M. E. Lipschutz[1]

Department of Chemistry
Purdue University

I. Introduction

One of the areas in which neutron activation has been widely applied is in the determination of trace element concentrations in geologic and extra-terrestrial (*i.e.* meteoritic) samples. Particularly in the case of meteorites these studies have been of the greatest aid in making deductions concerning the evolution of these objects and, by extrapolation, therefore of the solar system. However, these studies have also established that the meteorites differ considerably in composition and that even in samples of the same meteorite, differences in trace element contents by factors of 10-15 are often to be observed. Due to this compositional variability and to the fact that in almost all studies only one or two elements were measured in the same sample, the geochemical processes involved in meteorite formation are still quite obscure. Trace element measurements are particularly important since for these elements, small absolute effects result in large relative changes in elemental abundances. Thus, to establish a coherent picture of geochemical fractionation processes, it is necessary to measure the abundances of as large a number of elements as possible in the same sample. Ideally the elements to be measured should share the same physical and chemical properties but should differ in the degree of their response to external stimuli. They should also be present at trace element levels so as to maximize the effect of their response to external stimuli. Finally, they should represent as many of the four geochemical classes as possible, so as to allow a detailed unraveling of the complex geochemical history of the meteorites.

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[1] This research was sponsored in part by the U.S. National Science Foundation (Grant GA-1474) and the National Aeronautics and Space Administration.

In order to study the geochemical and geothermal history of stony meteorites we have determined to measure their contents of As, Sb, Bi, Tl, Hg, Ga, Ge, Os, Re, Te, Se, Sc, Co, Mo, Au, Cs and Zn. These elements were chosen because: a) they represent all but the atmophile class of elements in geochemical behavior; b) they are all volatile to a greater or lesser extent; and c) they are normally present in trace amounts (at the part per million (ppm) level. While, in principle, it would be possible to determine the concentrations of these elements by "classical" neutron activation techniques, in practice this is quite another matter. For this reason we have devised a novel adaptation of neutron activation which utilizes high-resolution gamma-ray detectors, a reirradiation technique for chemical yield determination and computer analysis for data reduction. We report here on the general description of our adaptation and on its test by its application to the analysis of geologic materials, namely the eight United States Geological Survey geochemical standards currently available.

II. Experimental Method

In our procedure two samples may be analyzed contemporaneously. The 0.5-2 g samples are sealed in quartz and are irradiated with appropriate flux monitors in the isotope tray of the Argonne CP-5 reactor for 6 days at a flux of about $8 \times 10^{12} \text{n} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$. After a one day cooling period the samples are then processed chemically.

A. CHEMICAL TECHNIQUES

Our technique is designed so as to minimize the elements' separation times. The irradiated sample is dissolved by HF and H_2SO_4 in the presence of carriers and the excess HF is converted into volatile BF_3 by addition of H_3BO_3. The solution is then made up to 6 N in HCl and is divided equally into two parts. The parts are then treated by the following group separation steps in order to extract three major groups of elements.

(1) One part is made up to 18 N in H_2SO_4 and is distilled by dropwise addition of HBr at 220 °C, using N_2 as a carrier gas. The volatile compounds of As, Sb, Hg, Os, Re, Se, and Te are collected and precipitated as sulfides. These sulfides are taken up in 10 ml of HCl-HNO_3 and 3 ml of this solution is counted.

(2) The second half of the solution is extracted with ether and after a few chemical steps Tl, Sb, Au, Mo, Ge, Ga and Te are separated. Again a 0.3 aliquot of this solution is counted. After the complete counting sequence Tl is separated by standard radiochemical techniques.

(3) The water-soluble portion of the second half is treated chemically in order to remove Bi. The remainder of this portion is passed through an

ion exchange column, and after several chemical steps, Sc, Co, Cs, and Zn are separated. Again a 0.3 aliquot of this solution is counted.

B. COUNTING TECHNIQUE

1. Beta Emitters

After purification of the Bi and Tl fractions by extensive radiochemical steps, so as to assure the absence of gamma-ray emitters, they are then counted in low level beta counters. The activity of the Bi fraction is followed for 5 half lives so as to assure that 5 day ^{210}Bi is radiochemically clean. The activity of 3.8 year ^{204}Tl is counted periodically over a several week period and then recycled to assure constant specific activity.

2. Gamma Emitters

The other elements are prepared for counting as separate groups by placing the aliquots in specially designed plastic containers and sealing them. Each sample is then counted under standardized and identical conditions with an 11.4 cm^3 coaxial Ge(Li) detector and a Packard Two-Parameter Analyzer which is operated in the 1024 single spectrum mode. These counts are repeated at specified intervals so as to observe the decay of short-lived nuclides. Each time, the spectrum is punched out on tally tape and stored. In addition, group flux monitors (which were irradiated together with the samples) are counted so as to establish the neutron flux experienced by the samples. All counts are taken in conjunction with a ^{207}Bi source whose gamma rays establish the calibration scale for the particular measurement.

When convenient (usually 1-3 weeks later) the chemical yields of the carrier are established by placing aliquots of the three groups in standardized sample containers and reirradiating these with suitable flux monitors for 10 minutes in the isotope tray of the CP-5 reactor. These samples are counted under the same conditions as were the original groups.

C. DATA ANALYSIS

In order to determine the elemental concentrations in the geochemical standards, counting data obtained at various specified intervals from the following sources must be used: (1) microgram amounts of pure elements irradiated for 6 days; (2) milligram amounts of pure elements irradiated for 10 minutes; (3) separated fractions of the originally activated geochemical standards (6 days) and associated flux monitors; and (4) reirradiated separated fractions of the activated geochemical standards (10 minutes) and associated flux monitors.

Obviously this procedure generates vast quantities of data which are most easily analyzed by computer. A series of programs including a linear least squares fitting program for the analysis of all gamma-ray spectra were written for the CDC-6500 computer. This program assumes that a sample spectrum is a linear combination of its component spectra. Information about all components present in a sample after irradiation is required to effect successful analysis of the data. The previous assumption holds true only if all component and sample spectra have a common gain and threshold. This is achieved by (1) compiling a self-consistent library of component spectra using the gamma rays of ^{207}Bi as an internal energy standard, and (2) allowing the fitting program to make coarse and fine adjustments to both gain and threshold.

III. Summary of Results

Rather than to attempt to give a complete summary of our results at this time, we have chosen to outline the method which we have developed. At present we believe it appropriate to note that we have analyzed, in duplicate, eight geochemical standards. In some cases more classical techniques have given reliable results with which we can compare our data. Where comparison is possible our results are in very good agreement with those obtained by other workers.

CHAPTER 5

INDUSTRIAL APPLICATIONS

Synopsis of Discussions

OSWALD U. ANDERS, *Chairman*

The Dow Chemical Company
Midland, Michigan

Industrial uses of neutron activation analysis are in their majority restricted to single element analyses in well-defined samples. Activation analysis for oxygen content of samples is used routinely by many companies. Possibly the outstanding example is at the Cockrill Steel Works in Belgium where up to 1500 analyses are carried out per week to control the oxygen content of the molten steel. Activation analysis for other elements which are difficult to do by the more classical methods such as the determination of fluorine, nitrogen in plastics and oils, *etc.* is being carried out in industry. However, most of these applications utilize accelerator neutron fluxes and analyze for constituents present in concentrations of .1 to 50%.

Rapidity and cost per analysis are important factors for routine industrial applications. This precludes many situations where chemical purifications of the activated sample would have been mandatory or a reactor flux needed to produce sufficient activity for counting.

It is pointed out on occasion that neutron activation analysis has not been accepted as readily by industry as have more recent analytical techniques such as vapor phase chromatography or atomic absorption, *etc.* The reasons are readily recognized as (1) the relatively small number of researchers which have been able and willing to develop neutron activation analysis and (2) the relatively expensive equipment needed for it.

But this picture is now rapidly changing. As industry purchases mass spectrometers and electron probe systems at costs exceeding $100,000—the costs for neutron activation analysis equipment appear more in line for a new analytical method. As more workers in the field become available (*re* the attendance at this conference) more practitioners will find their way into industrial laboratories. As the methods of neutron activation analysis are becoming more refined, more automated, and more sample independent so that they can be carried out by nontechnical personnel on a routine basis, the costs per determination will become more acceptable and the delays in sample processing time more manageable.

The presentations in the "Industrial Applications" session demonstrated both of these points. The work presented can be divided into two categories. The first contained papers illustrating typical applications of neutron activation analysis in industrial situations, utilizing more or less established principles of neutron activation analysis.

It was shown by the paper authored by L. Gorski and ably presented by Dr. Niewodniczanski how raw, crude oil, coming through the pipeline from oil fields in Northern European Russia to Poland is analyzed for its brine content. The authors used a 20th Century Electronics neutron generator with an output of 10^9 n/sec to induce ^{20}F, ^{16}N and ^{34}P in the crude oil in order to analyze Na, O and Cl respectively.

Dr. Gibbons reported results on wear studies in engines and a problem of ink transfer in the printing industry. The discussion revealed that oil filters in the engines which might have influenced the results by removing solid wear products, in practice plug up very early after installation in a typical automobile engine and are then bypassed and are effectively out of the system. Dr. Gibbons also pointed out that a search for iron in the oil will not reveal situations of excessive wear since this element would be readily found in the oil passing through an iron piping system. One better searches for a trace metal typical for the position at which wear occurs.

Prof. Iddings illustrated his presentation on the use of neutron activation analysis in the field to test freshly poured concrete, with a short movie demonstrating his ability of *in situ* analysis. The discussion revealed that a 5 curie isotopic neutron source of the type already used by highway departments to measure concrete moisture content might be used for on-the-road analyses of Ca.

Dr. Barber presented an illustration for the use of neutron activation analysis by the military for rocket fuel analyses. The relatively large errors obtained while using a more or less straightforward technique drew comments in the discussion. They were explained from problems encountered by the analyst when handling nonuniform samples.

Mr. Kuusi of Finland reported an application using neutron activation analysis in the mining industry in Scandinavia. Monitoring ^{28}Al and ^{52}V after 10 min activation of a 430 ml sample with a 3 curie ^{241}Am-Be neutron source, the equipment can follow the silicon concentration of chromium ore as well as its chromium content. The industrial set-up is capable of analyses with a 3% relative error.

Dr. Cosgrove gave us a status report on his effort to introduce neutron activation analysis at General Telephone and Electronics Laboratories, Inc. Based on hard economic facts the introduction of neutron activation analysis techniques has already replaced two x-ray fluorescence spectrometers as well as two atomic absorption units. At his company accelerator-based neutron activation analysis employed on a routine basis is able to compete favorably with more conventional methods. For difficult problems requiring reactor fluxes, he has the use of two reactors near his location where service irradiations can be purchased.

Dr. Marsh of the Ford Motor Company presented a project carried out by him using the Ford reactor at the University of Michigan illustrating the situation repeatedly encountered in our field when industrial neutron activation analysis is conducted with an outside reactor facility. The precision analyses of Na in ceramics using As as an internal standard proved a satisfactory, although somewhat expensive, experience in reactor based neutron activation analysis.

The second category of industrial neutron activation analysis illustrating industry's willingness to further advance the frontiers of the field when convinced of its usefulness was represented by the paper of Dr. O. U. Anders of the Dow Chemical Company. He reported a new approach to reactor-based, computerized and instrumental neutron activation analysis which was motivated by the need to make the method suited for automated multielement analysis on an economical basis. His approach which bypasses much of the developments in gamma-ray spectra fitting developed by physicists, concentrates on the essential needs of neutron activation analysis and may well provide a new direction for the field. An extended discussion clarified the details of his use of pulse-timing of the spectra to overcome the problems of pulse pile-up.

During the discussion session, Prof. W. Herr of the University of Cologne reported briefly about his work on the analysis of hafnium in zirconium. He used a coincidence technique to follow the decay of the 10-nanosecond ^{181m}Ta, probably the shortest lived nuclide thus far used for activation analysis.

The above comments were followed by a lively discussion concerning the economics of activation analysis in industry. The typical situations encountered in industry were identified as follows: (a) the industry owns the equipment for accelerator-based instrumental NAA and finds it economically sound in its present state, (b) the industrial company owns a reactor in addition to one or more small accelerators and expects that recent developments will make their usage of activation analysis economically sound in the not too distant future, (c) the company has available the use of a nearby nuclear facility whose services are sufficient and economical not to warrant duplication at their own site.

Depending on the stage and objective of their activation analysis program as well as on the know how represented by the employee carrying it out, neutron activation analysis is considered by industry as either faster, cheaper and more reliable; or expensive, slow and unreliable when compared to more classical methods of analysis.

Asked specifically to comment on the relatively unique support his project is receiving by the Dow Chemical Company, Dr. Anders was willing to make the following statement:

"The Dow Chemical Company is a growing company; it has about doubled in the last 15 years. It has a forward looking management open to new approaches. The Spectroscopy Laboratory has pioneered in the fields of x-ray spectrometry and infrared analysis since the 1930's. New techniques constitute a constantly developing area of interest and the philosophy of the company is that they ought to be current with the development and applications of these new techniques. If there is a breakthrough in one of the methods, it will be available; they have the method; they have the back-up for their production and research; and they don't have to stand back and wait until somebody else teaches them.

On the other hand I think that the expensive equipment is primarily justified by results. If you are successful in developing accelerator based activation analysis with a 2 MeV Van de Graaff accelerator over a period of 10-12 years and you have reached the limits of these methods and they are applied in the field, then the management looks favorably at the purchase of a reactor which can cost up to $250,000, and expects that you will produce similar results in the future. I have a strong feeling that we will be able to deliver and justify this expectation of us".

A list of the industrial users of neutron activation analysis was assembled with cooperation of many colleagues attending the conference. It is presented as an addendum to this synopsis.

Addendum to Snyopsis of Session on Industrial Applications

Companies using Neutron Activation Analysis
(probably incomplete)

UNITED STATES

Battelle Memorial Inst.	Pacific Northwest Lab. Richland, Washington	2 Reactors PETTZ FFTF (Future)
Boeing Aircraft Company	Seattle, Washington	accelerator
Chevron Research Company	Richmond, California	2 accelerators
Cyclotron Corporation	Berkeley, California	Cyclotron
Dow Chemical Company	Midland, Michigan	2 accelerators 1 TRIGA reactor
	Rocky Flats, Colorado	3 accelerators
Eastman Kodak Company	Rochester, New York	Cockcroft-Walton accelerator
Ford Motor Company	Dearborn, Michigan	use of Ford reactor at University of Michigan
General Telephone & Electronics Laboratories	Bayside, New York	Cockcroft-Walton accelerator-200 KV
Grumman Aircraft Engineering Corporation	Bethpage, L.I., New York	3 MV Van de Graaff 200 KV accelerator
Gulf General Atomic	San Diego, California	3 accelerators 3 TRIGA reactors
Gulf Research Corporation	Huntsville, Pennsylvania Pittsburgh, Pennsylvania	2 accelerators
IBM Corporation	E. Fishkill, New York	use Union Carbide Reactor, Tuxedo, New York
Industrial Reactor Labs.	Plainsboro, New Jersey	5 MW reactor
National Lead Company	Cincinnati, Ohio	1 Cockcroft-Walton accelerator
ORNL	Oak Ridge, Tennessee	14 MeV reactor
Phillips Petroleum Corporation	Bartlesville, Oklahoma	2 accelerators
PPG Industries	Corpus Christi, Texas	Cockcroft-Walton accelerator
RCA	Plainsboro, New Jersey	Reactor 5 MW
Reynolds Metals	Bauxite, Arkansas	isotopic neutron source
Shell Development Corporation	Emeryville, California	2 accelerators (use of TRIGA)
Tracerlab, West	Richmond, California	use various outside reactors
Union Carbide Corporation	Tuxedo, New York	5 MW reactor
Union Carbide Y-12 Plant	Oak Ridge, Tennessee	14 MeV
U.S. Steel (Research Lab.)	Pittsburgh, Pennsylvania	1 accelerator
Western New York Nuclear Research Center Inc.	Buffalo, New York	1 accelerator

Addendum (continued)

	FRANCE	
Atome Industriel	Grenoble	rents accelerator time and reactor time
ELF-UNION	Grenoble	uses facilities of the C.E.N. Grenoble
Pechiney Company	Grenoble	1 accelerator 1 lab. for radiochemical separations-using Grenoble reactor for irradiation
Radiotechnique	Saclay	uses facilities of the Center for Nuclear Studies at Saclay
Ugine-Kulhmann Company	Ugine and Paris	isotopic neutron source reactor irradiation
	JAPAN	
Hitachi Group	Kawasaki	shares jointly owned reactor facility among several industrial firms
Mitsubishi Group	Omiya	shares jointly owned reactor facility among several industrial firms
NAIG (Nippon Atomic Industrial Group)	Kawasaki	small nuclear reactor and Van de Graaff
Toshiba Electric Company	Kawasaki	accelerators
Yamata Steel Company	Kyushu District	1 accelerator (in production)
	GERMANY	
Gute Hoffnungs Huette Company	Essen	uses Belgian facility of Cockrill Corporation
IBM	Boeblingen	uses facilities of Kernforschungs-anstalt Karlsruhe
Siemens Company	Erlangen	1 accelerator
Wacker-Chemie	Munich	uses facilities of Institut fur Radiochemie, technische Hochschule Munchen (Reactor 5MW)
	SWITZERLAND	
Inrescor AG	P603 Schwerzenbad Zurich	? accelerator
	BELGIUM	
Cockrill Steel Corporation	Liege	1 accelerator (in production)
	DENMARK	
Haldor Topse	Copenhagen	using Riso Reactors

Addendum (continued)

SOUTH AFRICA

Iscor Steel Company	Pretoria, South Africa	14 MeV neutron generator

ITALY

ENI State Oil Company		reactor
Sorin Company	Saluggia, Vercelli	reactor facility jointly owned by Montecatini Co. and Fiat Co.

HUNGARY

Dunaujvaros Steel Company	Dunaujvaros	neutron generator

CANADA

Atomic Energy of Canada, Ltd. Commercial Products	Ottawa	3 Sb-Be 10^8 n · cm^{-2} · sec^{-1} isotope sources access to CRNL reactors
Dept. Energy, Mines & Resources	Ottawa	1 Cockcroft-Walton accelerator
Eldorado Mines, Ltd.	Port Hope	1 accelerator

ENGLAND

Aluminium Laboratories, Ltd.		rents accelerator at Harwell
GEC Rugby Semiconductor Company		uses facilities at Harwell
Guest Keene & Nettleforld Steel Company		accelerator
ICI Chemical Company		uses facilities at Harwell

NETHERLANDS

N.V. Philips	Eindhoven	1 variable-energy cyclotron 1 fixed " "
Reactor Centrum	Nederland Sponsored by the Dutch Industry	1 Argonaut reactor 1 M.T.R. reactor 1 neutron generator Texas Nuclear

FINLAND

Outokumpu Oy Research Lab.	Tapiola	isotopic neutron sources

Users of Neutron Activation Analysis Service of TRIGA Reactor Laboratory of Technical University Helsinki, Otaniemi

Central Laboratory Research Center of Pulp and Paper Industry	Tapiola	pulp and paper products
Neste Oy	Porvoo	petroleum products analysis
Outokumpu Oy, Central Lab.	Pori	metallurgical and mineral analysis
Tuppi Oy	Oulu	rare earth analysis
Valmet Ou, Rautpohja works	Jyvaskyla	paper coating and filler research

Several other smaller users, companies, hospitals, research laboratories, etc.

ON THE FEASIBILITY OF THE DETERMINATION OF WATER, SALT AND SULPHUR IN CRUDE OIL BY MEANS OF NEUTRON ACTIVATION ANALYSIS

L. Gorski, J. Janczyszyn, and L. Loska

Institute of Nuclear Techniques
Academy of Mining and Metallurgy
Krakow, Al. Mickiewicza 30, Poland

I. Introduction

Crude oil sometimes contains large amounts of water, salt and organic compounds of sulphur. These contaminations give rise to corrosion of distilling facilities and combustion engines.

To decrease the salt and water contents in crude oil the latter is subjected to gravitational separation in open basins. This process, however, does not give good results. Thus the necessity arises for continuous control of the salt and water contents in oil pipelines.

Contaminations of crude oil can be determined by means of activation analysis with 14 MeV neutrons. The contents of the particular contaminants in crude oil imported by Poland are the following: NaCl contents: small – 25 mg/liter, average – 250 mg/liter; exceptionally high – 1500 mg/liter; H_2O average – 6 g/liter; S average – 15 g/liter.

Continuous determination of these contaminations can be carried out on the basis of the reactions listed in Table 1.

II. Experimental

A. APPARATUS

A setup has been designed and constructed for preliminary measurements which confirmed the possibility of the determination of salt and water contents in crude oil. A schematic drawing of the setup is shown in Figure 1. The liquid prepared in the vessel A, is pumped into the vessel B, where it is activated for about 40 sec. From the vessel B, it gets through a pipeline into a measuring vessel C, through which it flows for about 50 sec. The activity of the liquid is measured by means of two 3 in. × 3 in. scintillation counters. The measurements were made using a 400-channel analyzer. The liquid was activated by 14 MeV neutrons from a NGH 150 neutron generator. The yield of neutrons was about 10^9

Table 1. Nuclear data of radioisotopes obtained during the activation of the determined elements.

Reaction	Cross section mb	Abundance percent	Half life	Gamma radiation MeV	Abundance percent
$^{16}O\ (n,p)^{16}N$	80	100	7.4 sec	6.14	69
$^{23}Na(n,p)^{23}Ne$	34	100	40 sec	0.44	33
$^{23}Na(n,\alpha)^{20}F$	220	100	10.7 sec	1.63	100
$^{24}S\ (n,p)^{34}P$	85	4.2	12.4 sec	2.13	25
$^{37}Cl(n,p)^{37}S$	30	24.6	5 min	3.1	90
$^{37}Cl(n,\alpha)^{34}P$	50	24.6	12.4 sec	2.13	25

neutrons/sec. The neutron output was monitored by means of a proportional counter of recoil protons.

The optimal rate of flow of the liquid was calculated requiring that the activity in the measuring vessel would be maximum. This activity is given by:

$$A = k\phi(1-e^{-\lambda t_i})e^{-\lambda t_t} \tag{1}$$

where:

k = is a constant
ϕ = the neutron flux
λ = the decay constant of the radioisotope measured
t_i = the irradiation time
t_t = the time of flow through the pipeline

The irradiation and flow times can be expressed by:

$$t_i = \frac{V}{Q};\ t_t = \frac{FL}{Q} \tag{2}$$

where:

V = volume of the activation vessel
Q = flow rate
F = area of the cross section of the pipeline
L = length of the pipe line.

Substituting (2) and (1) yields a formula for the activity from which one obtains the optimum flow rate:

$$Q = \frac{V\lambda}{\ln\left(1-\frac{V}{FL}\right)} \tag{3}$$

It was assumed that the neutron flux is time constant. The volume of the activation vessel B, was chosen so as to obtain a neutron flux at its walls amounting by about 10% of the maximum value. Figure 2 shows the cross section of the vessel, the shape of the neutron flux distribution [1], and the geometry of the target. The diameter of the pipeline should be the smallest possible; for technical reasons it was accepted as 1.5 mm.

Preliminary measurements were made with diesel oil instead of crude oil. The particular elements were added subsequently to the diesel oil as follows: oxygen in the form of a stearic acid ester (fat), sodium as an alcohol solution of sodium phenolate with the addition of toluene and

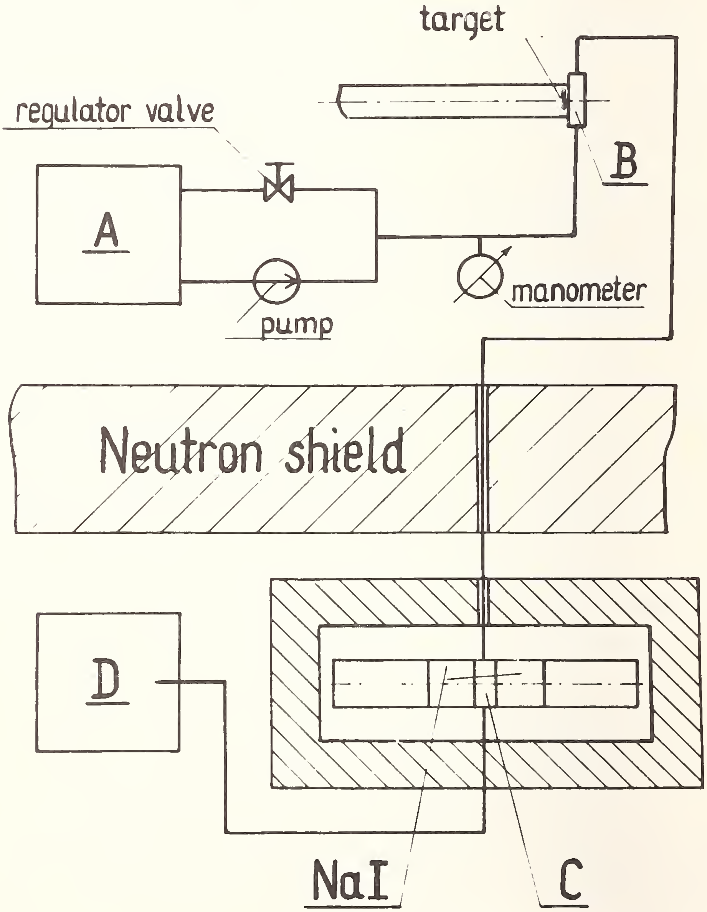

Figure 1. Schematic drawing of the set-up for the determination of water, salt and sulphur contents in crude oil.

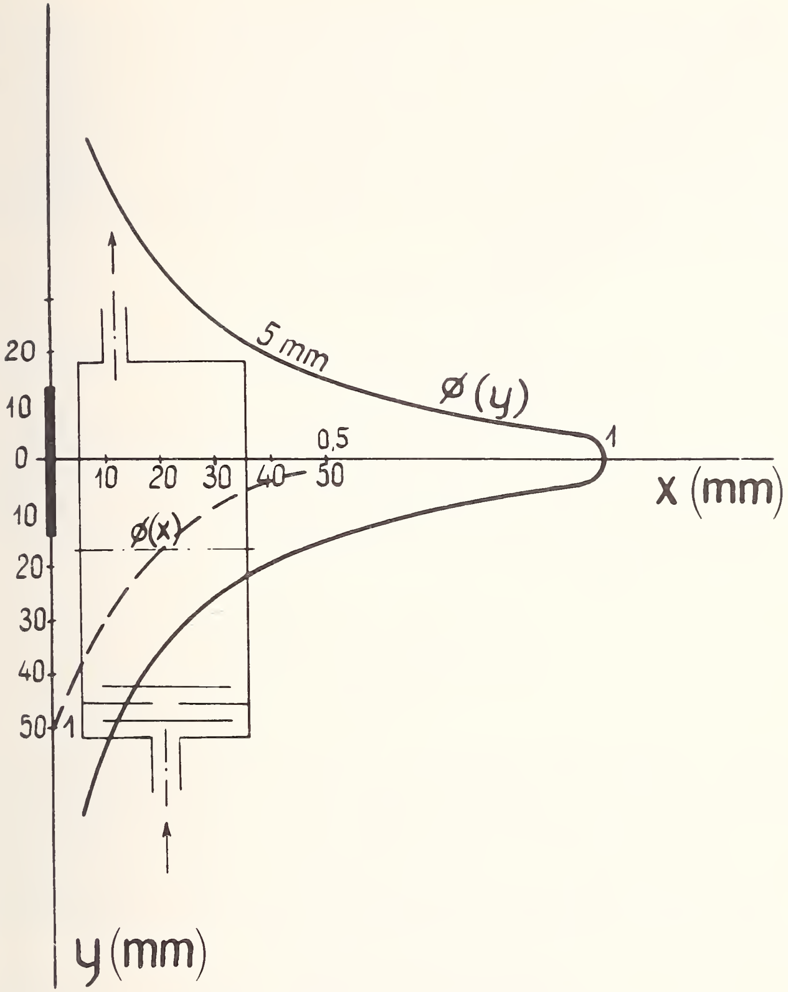

Figure 2. Distribution of the flux in the activation vessel.

sulphur in elementary form. The components used were chosen from the point of view of good solubility in oil and small volatility.

B. PROCEDURE

The experimental procedure was the following: 5 liters of diesel oil with known amount of the contaminating element were poured into the vessel A; then the pump was operated for the time needed to pump 2 liters of solution. During this time four subsequent measuring cycles were carried out: the neutron generator was switched on for 45 sec with the simultaneous measurement of neutron output; after this, the generator was switched off and the activity measured for 30 sec. Such a procedure was connected with the occurrence of a large background of high energy gamma quanta during the operation of the neutron generator. From the spectrum obtained in this way, the number of counts was calculated. The discrimination threshold for oxygen was 3.5 MeV. For sodium and sulphur the following formula was used for the calculation of the total number of counts in the peak:

$$N=N_p-\frac{N_i+N_k}{2}(k-i+1) \tag{4}$$

where:

$N_P =$ total number of counts in the interval of channels containing the peak

$N_i, N_k =$ the number of counts in the channels bounding the interval

The number of counts, N, was then normalized to the number of counts of the neutron monitor. The other measuring points for smaller concentrations were obtained by replenishing the investigated solution in the vessel A, with pure diesel oil.

III. Results and Discussion

A. RESULTS

Figure 3 shows the dependence of the total number of counts on oxygen content. The maximum oxygen content corresponds to the mean water content in crude oil. The straight line was fitted by means of the least squares method. It does not start at the origin of the coordinate system which is probably due to the presence of water in diesel oil. The concentration of oxygen corresponding to this water content can be determined from the plot; it amounts to 0.5 g/liter.

For the sake of comparison, a two minute measurement was made in the case of oxygen without switching off the generator. A considerable increase in statistical error was, in this case, the result of higher background.

Figures 4 and 5 show similar plots for sodium and sulphur, respectively.

B. DISCUSSION

In the case of oxygen and sodium the results seem to be very good, however, in the case of sulphur a determination by means of this method seems to be rather uncertain. It is possible that the choice of proper irradiation and measurement times and an increased number of measurement cycles should give better results.

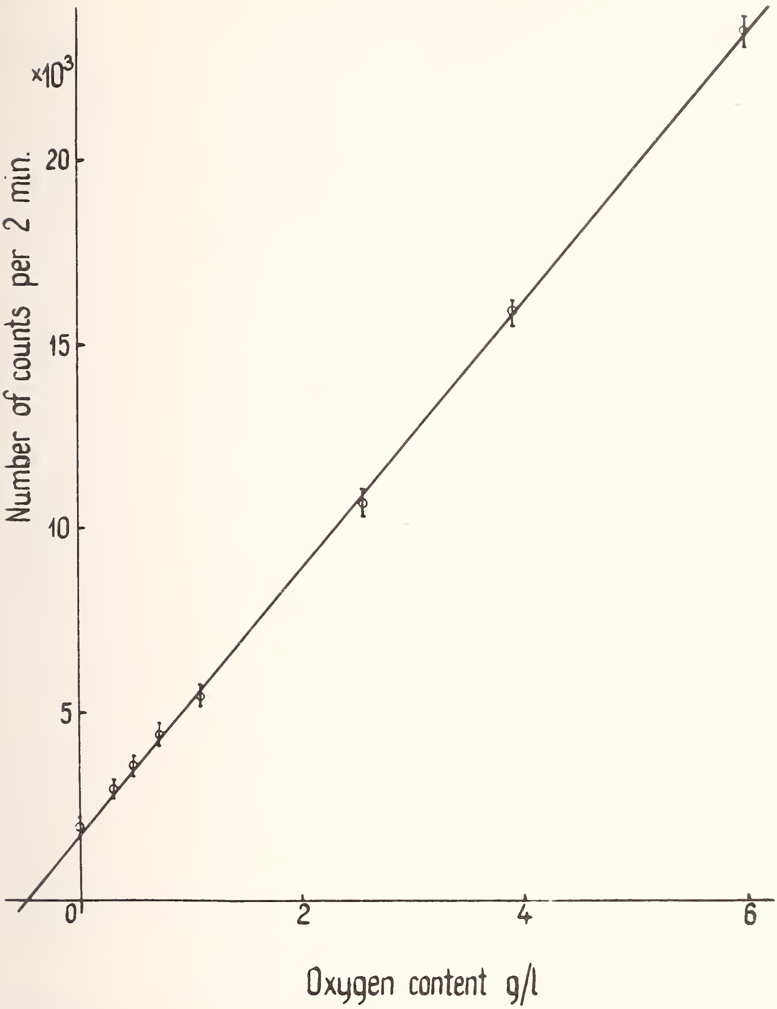

Figure 3. Dependence of the total number of counts on oxygen contents in diesel oil.

An attempt was made to determine sodium using the reaction $^{23}Na(n,p)^{23}Ne$. The 0.44 MeV peak obtained in this case is highly disturbed by the 0.511 MeV peak due to ^{13}N produced as a result of the reaction $^{13}C(p,n)^{13}N$. The spectrum obtained is shown in Figure 6. The measurement time was very long and amounted to about 50 min for each concentration. Because of this, it was decided that the determination of sodium is much more convenient on the basis of the reaction $^{23}Na(n,\alpha)^{20}F$. In this case the measurement time for each concentration is much smaller (about 5 min), while the numbers of counts in the peak are

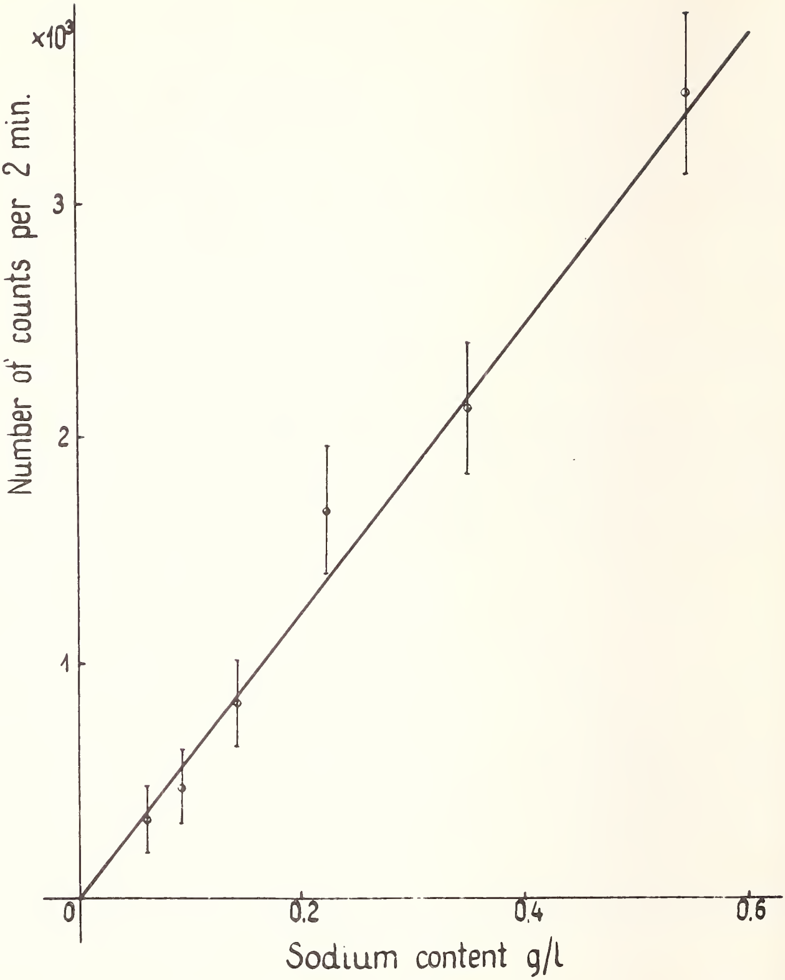

Figure 4. Dependence of the total number of counts on sodium contents in diesel oil.

comparable in both methods. It is worthwhile mentioning that determination of sodium in crude oil has been also made by means of thermal neutrons [2] and also by means of a discontinuous method [3].

No accurate check of the flow rate was made in the experiment. However, it follows from theoretical considerations that fluctuations of the flow rate occurring during the measurement, practically do not influence the accuracy of the measurement. Figure 7 shows the curves of the dependence of the activity of the liquid at the inlet of the measuring vessel C, on the flow rate. It can be seen that even a big change in the rate of flow results in an error of less than 1%.

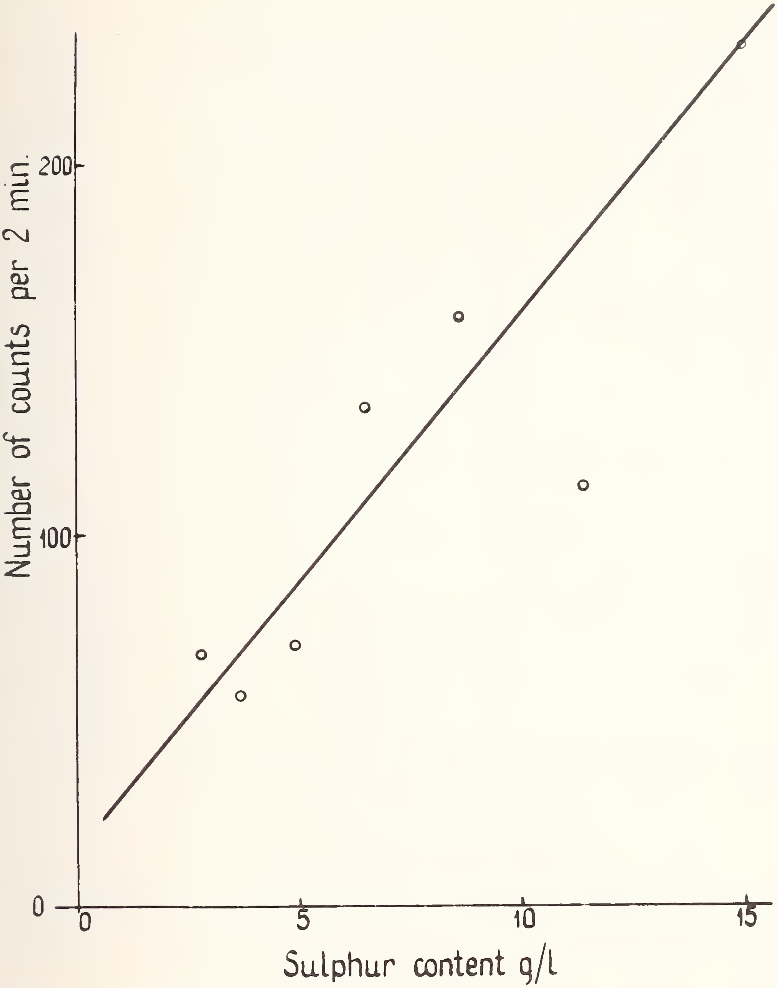

Figure 5. Dependence of the total number of counts on sulphur contents in diesel oil.

Considerable difficulties were encountered with the addition of sodium. The above mentioned solution mixtures used, contain volatile constituents whose evaporation leads to precipitation only after about two hours. Elementary sulphur can be dissolved in hot diesel oil up to 10 g/liter and crystallizes also after about two hours.

The final solution of the problem of the determination of mineral contaminations in crude oil should be possible, in the author's opinion, by means of a computer providing current results of the contents of water, salt and perhaps sulphur.

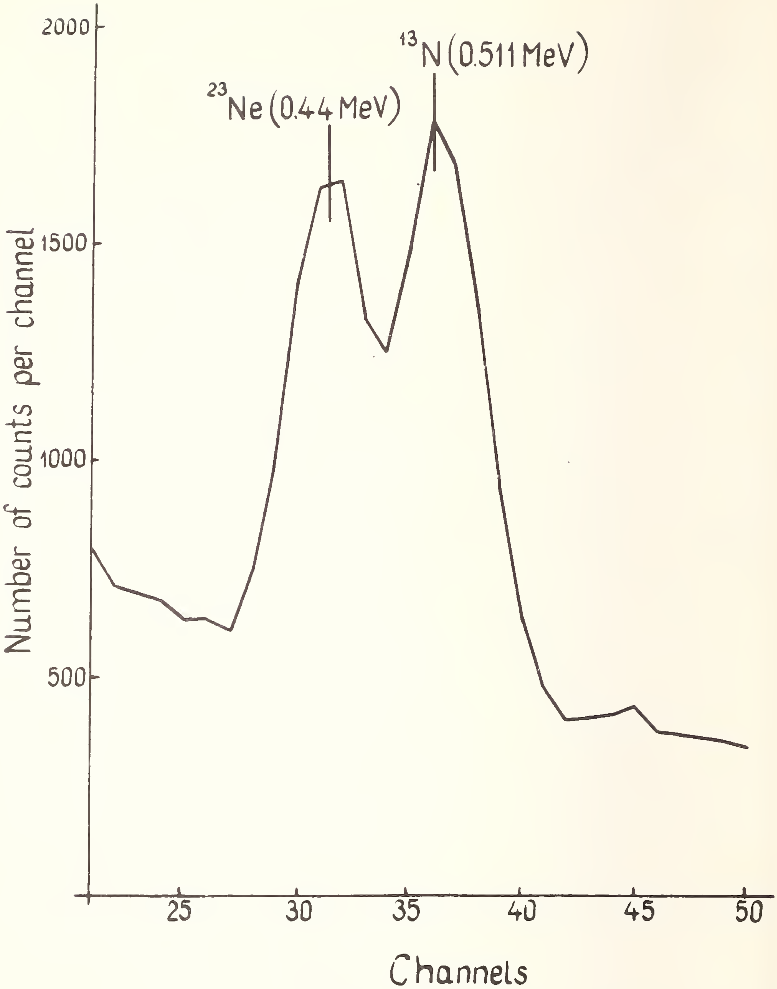

Figure 6. Spectrum of neon, ^{23}Ne and nitrogen, ^{13}N.

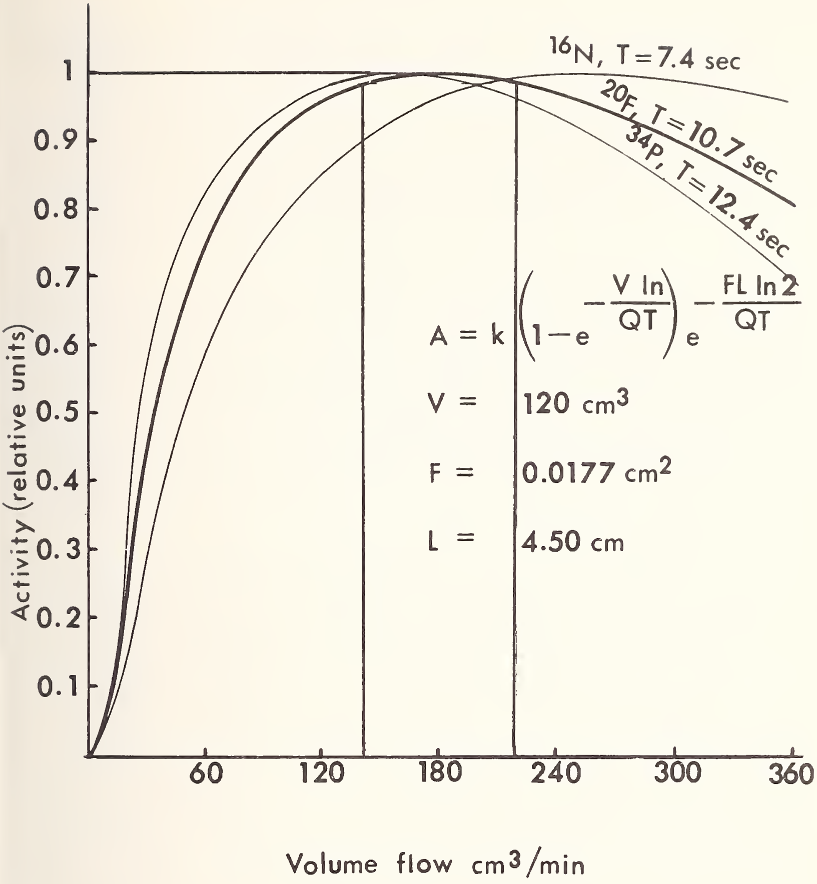

Figure 7. Dependence of the activity on the flow rate for different half lives.

IV. Acknowledgment

The work has been carried out under the IAEA Contract No. 375(RB).

V. References

[1] Hoste, J., DeSoete, D., Speecke, A., "The Determination of Oxygen in Metals by 14 MeV Neutron Activation Analysis". Belgian-Polish Symposium on Activation Analysis, Warsaw, September 1967.
[2] Braier, H. A., and Mott, W. A., Nuclear Applications **2**, 44 (1966).
[3] Iddings, F. A., Analysis Instrumentation, Plenum Press, New York, 1964, p. 139.

INVESTIGATION OF MATERIAL TRANSFER BY NEUTRON ACTIVATION ANALYSIS

D. Gibbons, D. Lawson, B. Metcalfe, and H. Simpson

Wantage Research Laboratory (AERE)
Wantage, Berkshire, England

I. Introduction

Radioisotope tracer techniques have become firmly established as methods for investigating material transfer [1-2]. In situations when only a small proportion of the labelled material is transferred, the amount of radioactivity needed as a tracer for the bulk from which it is transferred may be very large and radiation hazards may become a problem. As a result, special staff may need to be employed and the precautions involved may result in the system under investigation being operated under atypical conditions.

The use of an inactive tracer, followed by some form of analysis, offers a useful alternative provided that a suitable tracer can be found which is not present in significant quantities in the phase to which material is being transferred. In favorable circumstances this condition may be met by an existing constituent of the primary phase. No addition is then necessary and it is possible to operate the system without altering its characteristics.

Activation analysis is usually preferred to other methods of trace analysis in this context [3,4], because of the very favorable sensitivity for a wide range of elements and because of the inherent reliability and specificity even at concentrations approaching the limit of detection. There are some disadvantages to the activation analysis/inactive tracer method, however. The method is an elemental one and the transferred element is measured irrespective of its physical or chemical state, which might or might not be a disadvantage. Secondly, it is usually impossible to study a system in a true dynamic state, since samples must be removed for analysis and there will be some delay, depending on the element being measured, before the analytical results are available.

This technique has been used to investigate a series of material transfer problems. A typical selection is presented here, including both the use of an added inactive tracer and of a naturally occurring one.

II. Experimental

A. PRINTING INK TRANSFER

Control of ink thickness is desirable, particularly in lithographic processes where ink is transferred from etched rollers to paper, since the ink thickness affects not only the optical properties of the printed material, but also the potential printing speed.

As the ink in question was of an organic nature, an activatable tracer was added. Cerium naphthenate was used because it happened to be available and proved to be readily miscible with the ink. In practice, however, it proved to be easier to determine the ink thickness in terms of the lanthanum impurity (5% relative to cerium) in the additive rather than in terms of the cerium content itself.

Small areas of printed paper were irradiated for 24 hours at $10^{12} n \cdot cm^{-2} \cdot sec^{-1}$, together with printed paper and paper blanks and with "cerium" standards prepared by depositing known weights of cerium naphthenate on paper. After 4 days decay the lanthanum contents were determined by NaI gamma-ray spectrometry and compared with the depths to which the printing cylinders had been etched (Fig. 1). The measurements were then repeated for a variety of roller speeds and

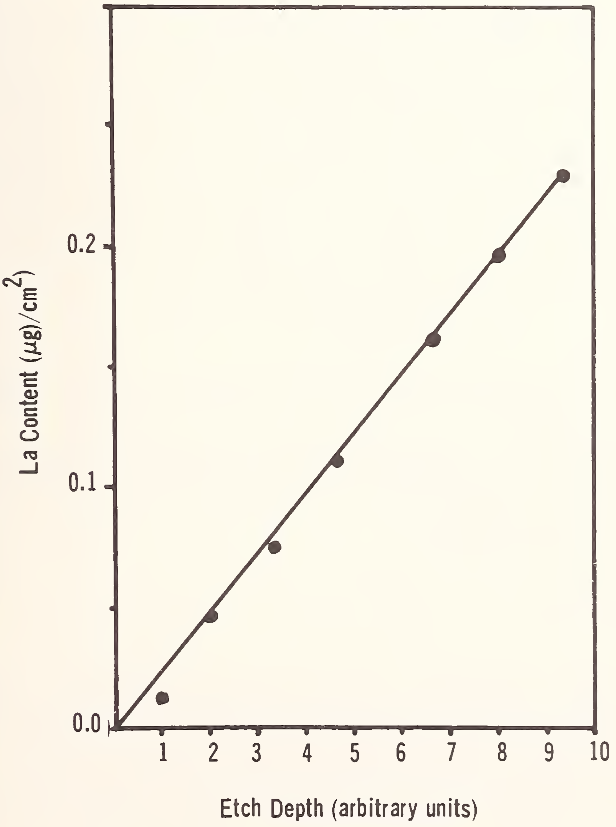

Figure 1. Lanthanum content of test prints.

pressures, and the lanthanum values compared with the theoretical value calculated from the cylinder etch depth (Table 1).

Table 1. Lanthanum content of printed areas under varying print conditions.

S P	T[a]	5A[a]	R	5B[a]	R	5C[a]	R	5D[a]	R	5E[a]	R
1	.066	.073	1.11	.057	.86	.061	.92	.060	.91	.055	.83
2	.132	.154	1.16	.155	1.17	.151	1.14	.148	1.12	.148	1.12
3	.220	.253	1.15	.237	1.08	.235	1.07	.209	.95	.230	1.05
4	.307	.343	1.12	.350	1.14	.352	1.15	.343	1.12	.322	1.05
5	.440	.395	.90	.413	.94	.415	.94	.400	.91	.361	.82
6	.527	.545	1.04	.525	1.00	.538	1.02	.530	1.01	.406	.77
7	.616	.610	.99	.615	1.00	.642	1.05	.607	.99	.573	.93
R			1.07		1.03		1.04		1.00		.94

S P	T[a]	5F[a]	R	6[a]	R	7[a]	R	8[a]	R
1	.066	.063	.95	.048	.73	.047	.71	.060	.91
2	.132	.140	1.06	.158	1.20	.140	1.06	.171	1.29
3	.220	.214	.97	.226	1.03	.239	1.04	.253	1.15
4	.307	.340	1.11	.345	1.12	.354	1.15	.384	1.25
5	.440	.384	.87	.402	.91	.392	.89	.438	.99
6	.527	.512	.97	.545	1.04	.552	1.05	.563	1.07
7	.616	.586	.95	.658	1.07	.598	.97	.655	1.07
R			.98		1.01		.98		1.10

Notes: T = Theoretical value calculated from printing cylinder etch depth
R = Ratio of observed lanthanum content to theoretical content
R = Mean value of R for a given set of print conditions
P = Print series
S = Etch depth no.

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[a] Values in μg.

It was thus established that the use of loaded ink, coupled with activation analysis offers a convenient method for the determination of ink film thickness. The method is limited by the availability of metal-organic compounds which are readily miscible with printing ink, but it should be possible to make similar measurements in multi-color processes.

B. Bearing Wear

The measurement of bearing or piston-ring wear using activated components is now a standard procedure [5], but in addition to the precautions necessary in handling the irradiated parts, it is usually necessary to limit testing to a special vehicle operating in a restricted area. The resulting wear is therefore not necessarily typical. By measuring wear products directly in samples of lubricating oil, no such restrictions are necessary but the method is then only a general one, and it is not possible to differentiate easily between different bearings.

It was found that for lead-indium shell bearings, wear could be measured in terms of the indium content of the lubricating oil. This was readily determined by a 10 min activation of a small sample of oil (less than 0.1% of the total oil present) at a neutron flux of 10^{12}n·cm^{-2}·sec^{-1} followed by nondestructive Ge(Li) gamma-ray spectrometry (^{116m}In 1.08 MeV, 54 min). The indium content of unused oil was shown to be negligible, and it was established that the wear due to 1 hour's running could be detected (Fig. 2). Wear was followed over a period of 500 hours and, apart from slight irregularities due possible to oil changes, the total wear was found to increase linearly with time (Fig. 3).

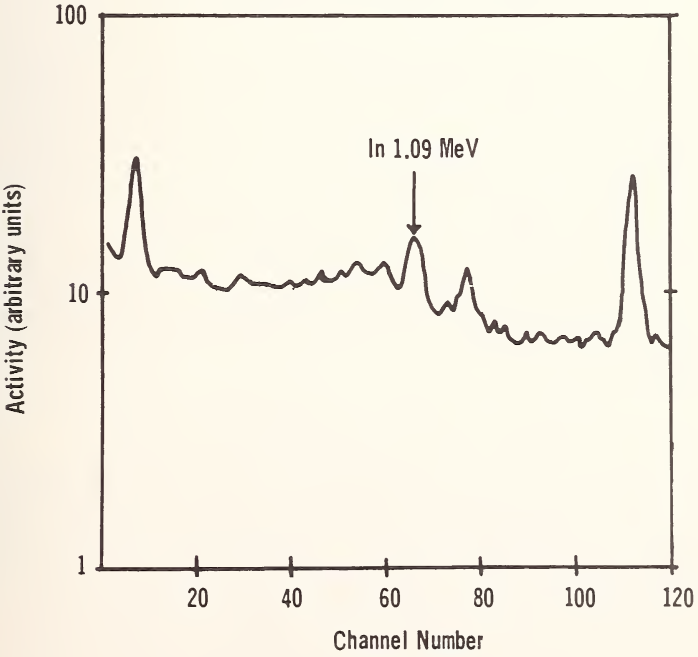

Figure 2. Ge(Li) gamma ray spectra of irradiated oil.

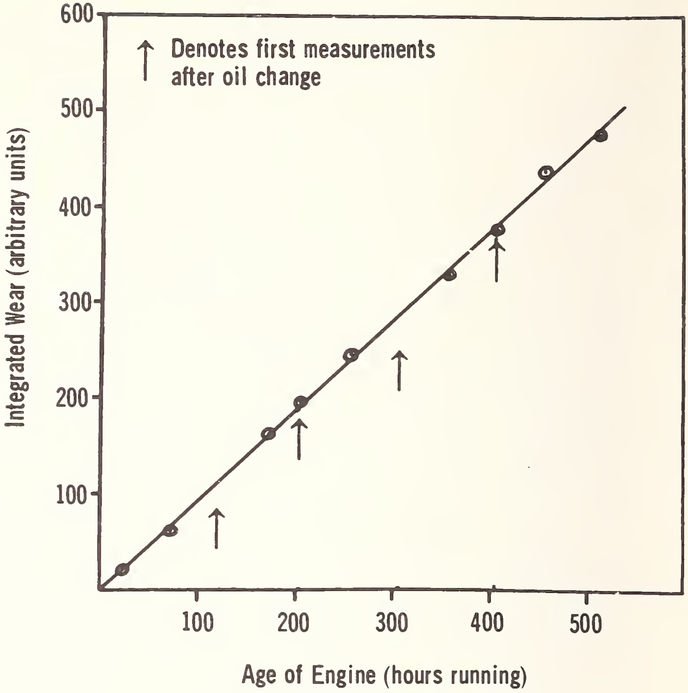

Figure 3. Rate of wear of Pb-In bearings.

The wear of aluminum-tin bearings is less easily studied by this technique since aluminum could be introduced into the oil from sources other than the bearings, and tin is less easily measured since its low energy gamma rays are swamped by those from bromine. (This element is found in used lubricating oil at concentrations as high as 0.2%.)

Although a suitable trace element could perhaps be incorporated in the bearing metal, it was desirable that the nature of the metal should not be altered. A separation scheme for the isolation of radiochemically pure tin is therefore being developed and the wear of the two types of bearings will be compared.

C. Coal Grinding Machinery Wear

Despite the very favorable sensitivity of activation analysis, the inactive tracer technique is sometimes difficult to apply when the secondary phase already contains a wide range of trace elements at concentrations greater than those likely to be introduced by wear. Such a difficulty arose when attempting to apply the technique to the measurement of the wear of coal grinding machinery where it was estimated that the *total* wear debris in the coal after pulverization would be about 1 ppm. Most of the elements suitable for use as tracers could not be introduced into the wearing parts at a concentration greater than 0.1%. It was therefore necessary to establish which elements with convenient nuclear characteristics for activation analysis were present in coal at concentrations below about 10^{-9}g/g.

Preliminary instrumental analysis of a variety of coals by NaI gamma-ray spectrometry revealed substantial concentrations of Na, Mn, Cl, As, Cu, Cr, La, Sc, and Fe which ruled out the use of these elements as tracers. The general level of activity also prevented the instrumental detection of tracers such as Co, Ta, W, Re, Ir, and Au with the required sensitivity, and radiochemical separations (Table 2) were therefore

Table 2. Radiochemical schemes for use after oxidation of coal samples.

Gold	Tungsten	Rhenium
Reduce with SO_2 Dissolve in dilute aqua regia Extract with ethyl Ac Evaporate to dryness Dissolve in dilute aqua regia Dilute with water Add hydroquinone Weigh as Au Measure at 0.41 MeV	Evaporate with H_2SO_4 Boil with HCl Collect HWO_3 Dissolve in ammonia Scavenge with Fe Add $NH_4CNS/SnCl_2$ Extract with ether Evaporate over HNO_3 Weigh as HWO_3 Measure at 0.48 MeV	Precipitate with H_2S Dissolve in H_2O_2/NH_3 Scavenge with Fe Precipitate with tetraphenyl arsonium-chloride Weigh precipitate Measure at 0.14 MeV

Iridium	Tantalum	Cobalt
Boil with HCl Centrifuge Adjust solution to pH 5.7 Separate Ir oxide Dissolve in aqua regia Scavenge with Fe Acidify Precipitate Ir with Zn Weigh as Ir Measure at 0.32 MeV	Boil with HCl Separate Ta Dissolve in H_2SO_4/HF Extract with methylisobutyl ketone Back extract with dilute H_2O_2 Neutralize and boil Dissolve in H_2SO_4/HF Precipitate with tri-2.2 -dipyridyl ferrous-sulphate Weigh Measure at 1.2 MeV	Boil with HCl Precipitate Ir at pH 5.7 Centrifuge Scavenge with Fe Add H_2O_2/ammonia Dissolve $Co(OH)_3$ in HCl Add HAc and KNO_2 Precipitate $K_3Co(NO_2)6$ $K_3Co(NO_2)6$ Weigh Measure at 1.33 MeV

developed for their purification. These were simple schemes intended only to provide sufficient radiochemical purity in each case to permit reliable gamma-ray spectrometry. These procedures were applied to what appeared to be the purest coals, but in no case was a concentration measured which was adequately low to permit wear measurements to be made (Table 3).

Table 3. Trace element content of coal.

	Cobalt	Iridium	Tungsten	Rhenium	Gold	Tantalum
Coal A[a]	23	5×10^{-3}	2×10^{-2}	7×10^{-3}	3×10^{-3}	4×10^{-1}
Coal B[b]	⊀	⊀	⊀	6×10^{-3}	2×10^{-2}	⊀

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[a] In parts per million.

[b] ⊀ not measured.

III. Conclusions

The use of activation analysis for the study of material transfer avoids some of the problems associated with radioactive isotopes as tracers. However, the method is limited when the nature of the secondary phase makes detection of the wear products difficult, or when physical requirements preclude the incorporation of a sufficiently unusual element in the primary phase.

IV. References

[1] Erwall, L. G., Forsberg, H. G., and Ljunggren, K., Industrial Isotope Techniques, Munksgaard, Copenhagen, 1964, p. 164.

[2] Piraux, H., Radioisotopes and their Industrial Applications, Cleaver-Hume, 1964, p. 182.

[3] Schultz, W. W., Briggs, H. D., Dewes, R. A., Godale, E. E., Morley, D. H., Neissel, J. P., Rochlin, R. S., and Verbinski, V. V., Proc. 2nd United Nations Conf., Peaceful Uses of Atomic Energy, Vol. 19, United Nations, Geneva, 1958, p. 112.

[4] Radwan, M., Reveiska-Kostook, B., and Vezranovski, E., Proc. IAEA Symposium, Radioisotope Tracers in Industry and Geophysics, IAEA, Vienna, 1967, p. 71.

[5] Deterding, J. H., and Calow, J. R. B., Proc. 2nd United Nations Conf., Peaceful Uses of Atomic Energy, Vol. 19, United Nations, Geneva, 1958, p. 141.

APPLICATIONS OF ACTIVATION ANALYSIS TO DETERMINATION OF CEMENT IN CONCRETE

F. A. Iddings and Ara Arman

Louisiana State University
Baton Rouge, Louisiana 70803

I. Introduction

The control of concrete and soil-cement mixtures has gained new significance as the result of more critical stress limits in structural engineering and the approach of idealized strength and quality in modern construction. The engineer must be assured of the composition, mixing, placing and curing of concrete, the strength and attendant qualities of which vary directly with the cement content and uniformity of cement distribution in the mixture [1].

Chemical analyses for determining cement composition are slow and tedious, and are thus ill-suited for field use. All of the problems related to such tests, such as dissolution of the sample, nonrepresentative results from small samples, and the need for skilled operators, prevent chemical analysis from providing the necessary data before the concrete has set and cured in place. Activation analysis appears to offer the speed, accuracy, ruggedness, and the simplicity of operation necessary to provide the construction engineer with the desired information in the field.

This paper describes laboratory and field studies that utilized fast and thermal neutron activation coupled with NaI(Tl) and Ge(Li) detectors.

II. Laboratory Work

A. Apparatus and Reagents

Laboratory Accelerator: Texas Nuclear Corporation Model 9500 with 1 curie/sq. in. tritium targets.

Portable Field Accelerator: Kaman Nuclear Corporation Model A-700.

Nuclear Reactor Facility: Georgia Institute of Technology heavy water reactor, flux used was 8×10^{12} n·cm^{-2}·sec^{-1}.

3 in. × 3 in. NaI(Tl) Harshaw Integral Line Detector, with 7.6% resolution for cesium-137, and 100 and 400 channel TMC analyzers.

16 cm^3 Ge(Li) Ortec Detector with 1024 channel analyzer, Nuclear Data Model 2200.

100 V AC Portable generator, Sears Roebuck Model 580.3199.

B. PROCEDURE

Samples of cement, concrete, sand and aggregate, soil, and soil-cement mixtures were activated by 14 MeV neutrons from the accelerator or by thermal neutrons from the nuclear reactor. A variety of activation, decay, and count times were used in unsuccessful efforts to discover a unique component in cement that would offer a good method for activation analysis.

However, because the calcium content of Portland cement is relatively high compared to that of the usual aggregate (sand and gravel); and, similarly, the silicon content of the aggregate is much higher than that of the cement. Silicon and calcium seemed to be the most indicative elements for obtaining a usable response to activation. Calcium produces the short-lived isotope Ca-49 ($T_{1/2} = 8.8$ minutes, 3.08 and 4.06 MeV gamma rays) from thermal neutron activation; silicon produces the short-lived isotope Al-28 ($T_{1/2} = 2.3$ minutes, 1.78 MeV gamma ray) from fast (14 MeV) neutron bombardment (Figs. 1 and 2).

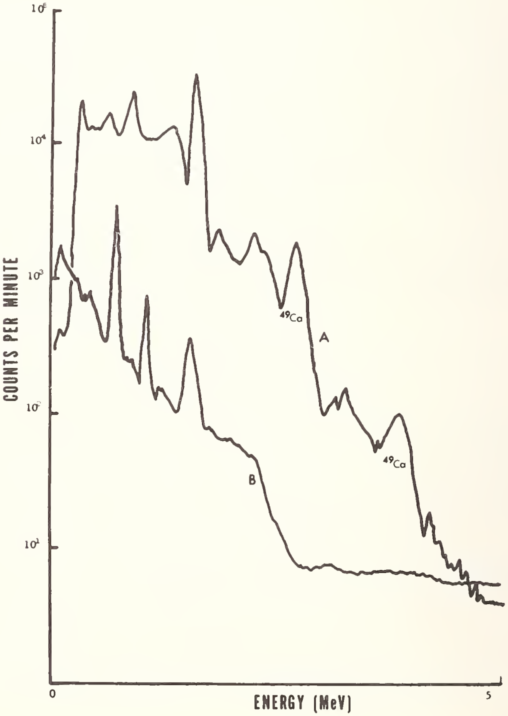


Figure 1. Gamma spectra of (n,γ) thermal neutron products in concrete for 10 seconds at 8 × 10^{12} n·cm^{-2}·sec^{-1}. Curve A – 9 min decay; Curve B – 8.5 h decay.

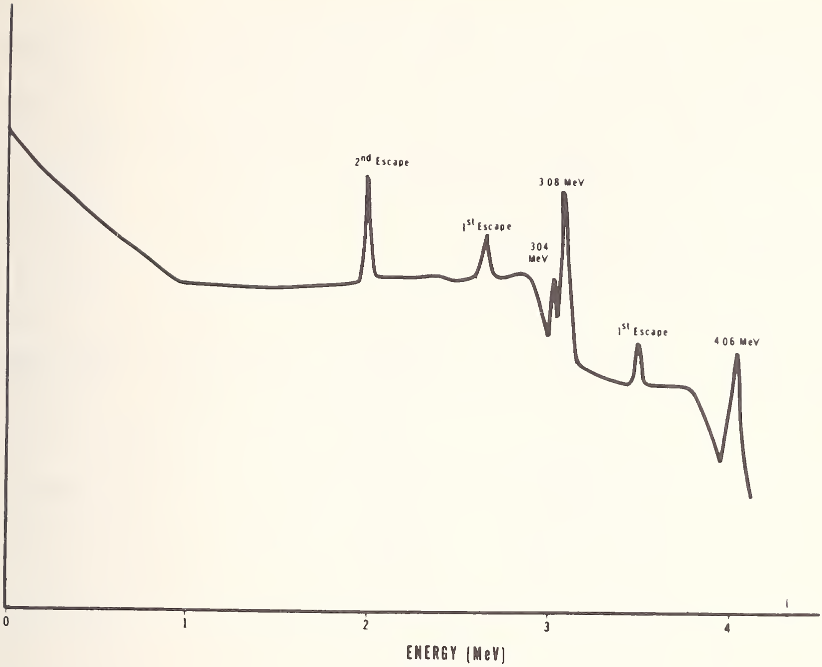


Figure 2. Typical Ge(Li) gamma-ray spectrum from concrete samples activated for 1 second, decay for 720 seconds, and counted for 400 seconds. Lead absorber 1/8 inch thick placed around sample.

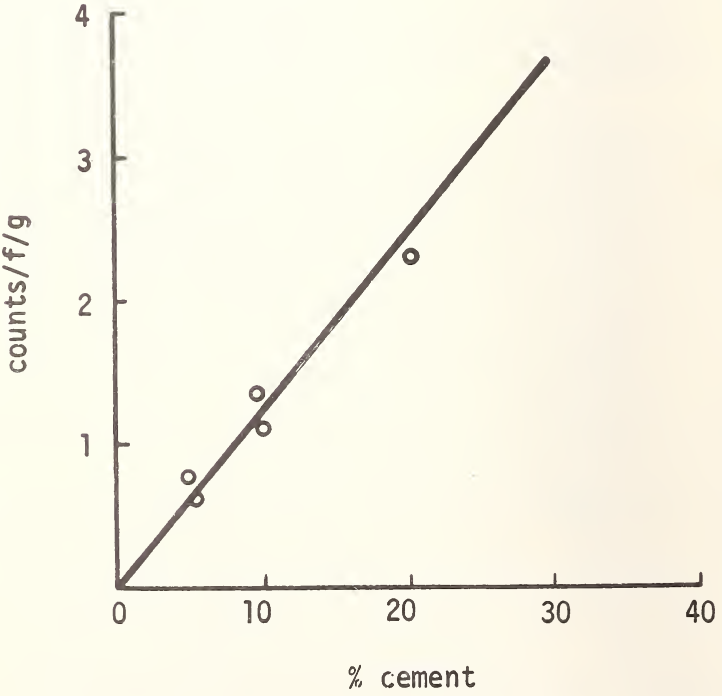
Only the short-lived products were used in this study because a rapid method of analysis was desired. Because longer activation periods produced complex radioactivity, thermal neutron activations of only 1 second followed by a 720 second decay period and a 400 second counting period with a Ge(Li) detector gave the best results. Flux wires of 0.1% gold-in-aluminum were used to correct for activation time. Samples larger than 1 cm^3, with which the available 8×10^{12} n·cm^{-2}·sec^{-1} flux was used would be advantageous in that lower fluxes available from isotopic neutron sources could be used. Results from the calcium determination by thermal neutron activation gave a practical calibration curve. Similar results have been found by Covault and Poovey [2].

Silicon determination using fast (14 MeV) neutrons was also tried as a measure of cement concentration. Since Portland cement concrete is mostly gravel and sand, the silicon concentration decreases with increasing cement concentration. However, with the crude arrangement used, the necessary precision was not obtained. Better sample positioning, and possibly sample rotation during the activation would help. The best data obtained in the laboratory was gotten from samples with glass plates attached as flux monitors (Table 1). Vincent and Volborth [3] obtained a precision of ± 0.12% Si at the 40% Si level which would be sufficient for most engineering analytical support.

Table 1. Thermal neutron activation analysis results on concrete samples.

Procedure: 1 second activation
720 second decay
400 second count

Run No.	Sample	Weight (grams)	Counts/g (corrected for neutron flux)
2	sand	1.937	0.0
3	5% cement	3.048	0.788
8	5% cement	2.796	0.640
4	10% cement	2.625	1.35
7	10% cement	2.820	1.09
5	20% cement	2.718	2.26



III. Field Work

A part of the studies involved the feasibility of using a portable fast neutron generator and associated counting equipment in the field. The field work was done with a specially mounted Kaman Nuclear Corporation Model A-700 accelerator. The special platform held the accelerator in a vertical position so that after an area of highway had been bombarded with 14 MeV neutrons, the accelerator could be quickly moved aside for the counting of the induced aluminum-28 activity from $^{28}Si(n,p)^{28}Al$. This accelerator was operated in the open without shielding other than the 50-foot distance provided by long cables between the control unit and accelerator. Only 30 second activations were used. No measurable radiation exposure to personnel was found under the operating conditions (Figs. 3 and 4).

A 5 in. × 5 in. glass plate placed over the area to be activated acted as a flux monitor. The plate was counted after a 1 minute decay. The soil or concrete area was counted after a 3 minute decay. The counting was done with a 3 in. × 3 in. NaI(Tl) crystal kept in a 1 gallon polystyrene thermos jug. (The thermal and shock insulation provided the protection and stability necessary for field use). High voltage was supplied by a battery pack. A portable, gasoline-driven 110 V AC generator powered the accelerator, the multichannel analyzer, and the printer. The multichannel analyzer required an air-conditioned automobile for best operation under

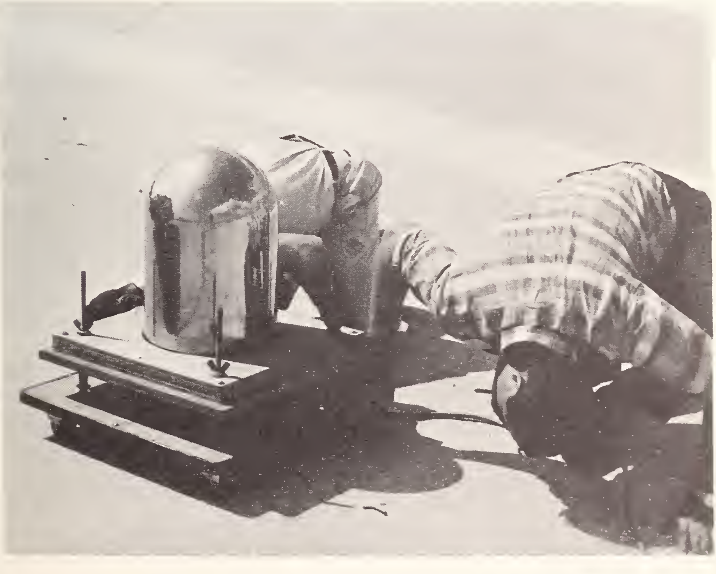


Figure 3. Positioning of portable 14 MeV neutron generator in field fast neutron activation analysis.

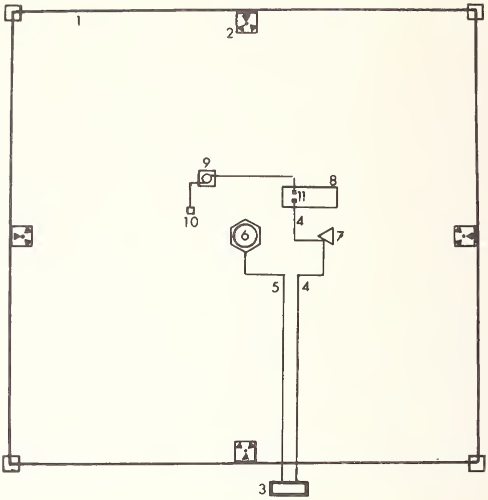


Figure 4. Layout for performing fast neutron activation in the field. 1. Rope; 2. Radiation signs; 3. Remote control console; 4. A.C. cables; 5. Control cable; 6. Neutron generator; 7. A.C. generator; 8. Air conditioned station wagon; 9. Detector; 10. Battery pack; 11. Counting equipment.

field conditions in the summer. All the equipment fitted easily into the back of an air-conditioned station wagon. The equipment operated satisfactorily under field conditions. Whether the necessary precision can be obtained has not been established, as yet because the analyses to check the field data were not available (Table 2).

Table 2. Results of field irradiation using portable neutron generator on concrete roadway.

Samples	Decay time	Net ^{28}Al photopeak counts	Ratio: $\frac{^{28}\text{Al counts in sample}}{^{28}\text{Al counts in glass}}$
Concrete	3.5 min	19471	5.37
Glass	2 min	3627	
Concrete	3.5 min	17420	5.05
Glass	2 min	3455	
Concrete	3.5 min	23919	4.12
Glass	2 min	5812	
Concrete	3.5 min	14371	5.51
Glass	2 min	2610	
Concrete	3.5 min	21469	4.55
Glass	2 min	4717	

Neither the same spot of concrete nor the same glass plate was irradiated twice.

(The flux monitor used was 5 in. × 5 in. double strength glass.)

IV. Conclusions

This work shows that the best approach to cement determination in concrete by activation analysis is through thermal neutron activation. This should be possible using isotopic neutron sources in a howitzer for the activation of large samples. The use of such sources is familiar to many construction engineers since neutron moisture gauges have become commonplace.

No problems were encountered with the counting equipment. This is no surprise because similar equipment is truck-mounted for prospecting. Whether the precision of the silicon content determined from 14 MeV neutron activation is sufficient for cement determination remains to be seen. Silicon determination would be necessary if the concrete aggregates are calcareous (high calcium content, such as shell).

The determination of either calcium or silicon by activation analysis would be rapid enough to prevent the pouring and curing in place of a bad batch of concrete. Speed is as essential as accuracy in cement determination, because test results obtained even a few hours later do not permit correction of concrete that has already set.

V. Acknowledgments

The authors recognize and appreciate the experimental work performed by A. W. Perez, II and D. W. Kiesel and the support by the Louisiana State Department of Highways in cooperation with the U.S. Department of Transportation, Federal Highway Administration, Bureau of Public Roads.

VI. References

[1] Blaine, R. L., Arni, H. T., and Foster, B. E., "Interrelations Between Cement and Concrete Properties, Part 1" Department of Commerce, U.S. Government Printing Office, 1965.

[2] Covault, D. O., and Poovey, C. E., "Use of Neutron Activation to Determine Cement Content of Portland Cement Concrete". Highway Research Board Bull. No. 340, 1-29, 1962.

[3] Vincent, H. A., and Volborth, A., Nuclear Appl. **3**, 753 (1967).

[4] Heath, R. L., "Scintillation Spectrometry", IDO-16880 U.S.A.E.C. (August 1964).

[5] Hosticka, H. A., "Radioisotopes and Nuclear Reactions Applied to Soil Mechanics Problems", ASTM Special Tech. Publ. No. 134, 1952.

DETERMINATION OF SODIUM AND POTASSIUM IN SOLID PROPELLANTS

W. H. Barber and O. H. Dengel

Naval Ordnance Station
Indian Head, Maryland 20640

R. H. Vogt and C. V. Strain

Naval Research Laboratory
Washington, D.C. 20390

I. Introduction

Recent developments in the field of solid rocket propellants require an analytical method to determine trace amounts of sodium and potassium in a solid propellant matrix. The technique of neutron activation analysis was selected because of its excellent sensitivity, precision, and reasonable accuracy. For this particular application, the neutron activation analysis technique has the additional advantage of nondestructiveness through the use of gamma-ray spectroscopy.

According to the reaction $^{23}Na(n,\gamma)^{24}Na$, sodium, when exposed to a thermal neutron flux, forms radioactive ^{24}Na which decays by emitting two gamma rays with energies of 2.754 MeV and 1.369 MeV, respectively. The $^{27}Al(n,\alpha)^{24}Na$ and the $^{24}Mg(n,p)^{24}Na$ reactions can interfere with the primary reaction, $^{23}Na(n,\gamma)^{24}Na$. The activation cross section for the $^{27}Al(n,\alpha)^{24}Na$ reaction is 0.6 mb, while the reaction $^{24}Mg(n,p)^{24}Na$ has an activation cross section of 1.3 mb. These cross sections are almost three orders of magnitude smaller than the 0.53 b cross section of the $^{23}Na(n,\gamma)^{24}Na$ reaction.

For the solid propellant analyzed in this study no magnesium could be detected. However, as many solid propellants contain aluminum, it is evident that serious difficulties will arise for any trace sodium determination unless special precautions are taken. Techniques have been developed, using a specially designed thermal column that effectively suppress the $^{27}Al(n,\alpha)^{24}Na$ interference.

For the determination of trace amounts of potassium, the thermal neutron reaction $^{41}K(n,\gamma)^{42}K$ was used. Interferences with this reaction may result from the reactions $^{42}Ca(n,p)^{42}K$ and $^{45}Sc(n,\alpha)^{42}K$. However, since no scandium and only trace amounts of calcium were detected in the propellants, these two competing reactions could be neglected.

II. Experimental

A. Sodium Determination

1. Apparatus

For the determination of sodium, the propellant samples were irradiated in the thermal column of the Naval Research Laboratory's one megawatt swimming pool research reactor [1]. The thermal column of this reactor has a maximum available thermal neutron flux of 10^{10} $n \cdot cm^{-2} \cdot sec^{-1}$ and a cadmium ratio of 470. Using this thermal column, sodium determinations at the 1-10 part per million (ppm) level can be achieved for aluminized (10-20% aluminum) propellants.

2. Procedure

One gram propellant samples sealed in polyethylene vials were irradiated for at least seven hours in the thermal column. In order to minimize any thermal neutron flux gradient in the thermal column, the samples were rotated uniaxially at 60 rpm. Following irradiation, the samples were allowed to cool for approximately 15 hours to permit all short-lived radioisotopes to decay to insignificance. Each sample was then counted ten minutes with a 3 in. × 3 in. NaI(Tl) detector coupled to a 400 channel pulse-height analyzer. The data were punched on paper tape and subsequently evaluated with the aid of a Honeywell 2200 computer.

B. Potassium Determination

For the determination of potassium in solid propellant samples, a separate irradiation at a position of higher thermal neutron flux was required to maintain the desired sensitivity. This difficulty was created because the isotopic abundance of the stable isotope, ^{41}K, is only 6.77% [2] and the branching ratio of the major gamma ray for the radioisotope, ^{42}K, is only 18%. Thus, although the thermal activation cross section for the $^{41}K(n,\gamma)^{42}K$ reaction is 1.2 b, the sensitivity for potassium using thermal neutron activation analysis is approximately 30 times less than that for sodium.

1. Apparatus

To maintain a reasonable sensitivity for potassium, the propellant samples were irradiated in glory tube 2A of the NRL reactor. At this position, the thermal neutron flux is on the order of 6×10^{12} $n \cdot cm^{-2} \cdot sec^{-1}$, or approximately 200 times greater than the thermal neutron flux available in the thermal column.

2. Procedure

One gram propellant samples were sealed in polyethylene vials and irradiated in the glory tube for periods ranging from four to five hours. To help suppress any thermal neutron flux variations in the glory tube, all propellant samples were rotated uniaxially at 20 revolutions per minute. Following a cooling period of at least 15 hours to permit short-lived radioisotopes to decay to insignificance, the samples were counted for 40 minutes each with a Ge(Li) solid state detector.

Because of the greater fast neutron flux available in the glory tube, the ^{24}Na formed from the ^{27}Al(n,α)^{24}Na reaction becomes the major radioisotope present in all propellant samples. This interference excludes the use of a NaI(Tl) detector for use in sample evaluation because of its poor resolution characteristics (± 7.4% at 661 keV). The main peak of ^{24}Na, 1.369 MeV, would overlap the main peak of ^{42}K, 1.524 MeV, thus necessitating a spectrum stripping technique with its corresponding inaccuracies.

This difficulty was overcome by using a Ge(Li) solid-state detector of 40 cm^3 volume with a resolution of 4.7 keV and a 4096 channel multichannel analyzer. Using this combination, the two peaks were easily resolved, and the spectrum stripping operation could be eliminated. Sample spectra from the 4096 channel analyzer were dumped on magnetic tape. These tapes were subsequently evaluated using a Honeywell 2200 computer.

III. Results and Discussion

A. RESULTS

Using the technique described above, eight batches of Sidewinder-1C solid propellant were selected and analyzed for sodium and potassium content. The results of this study, normalized for decay, weight, and duration of irradiation, are presented in Table 1. Sodium determinations appear in Table 1 and potassium results may be found in Table 2.

B. DISCUSSION

From the results shown in Table 1, it is evident that a thermal neutron activation analysis technique provides an accurate, reliable method for determining sodium and potassium in aluminized solid propellants. Because of its inherent nondestructiveness for this application, the activation analysis technique introduces no extraneous sodium or potassium impurities into the samples that might impair the final results. Finally, since all samples were evaluated under a 2σ confidence interval,

Table 1. Sodium in sidewinder propellant.

	Sample number			
	O124–96Q	O124–96M	O124–96A	Q124–96F
Counts/h/g	435758	468025	343166	249917
	491317	485083	304021	224692
	417982	472256	300896	225723
	485070	427237	324273	237824
	442728	505570	356444	238856
	468046	433998	358835	200514
	487407	485356	313628	221272
			346335	208693
Irradiation time	7 h 15 min	7 h 10 min	7 h 45 min	7 h 25 min
Counting time	10 min	10 min	10 min	10 min
$\bar{N}$	461187	468218	330950	225936
2σ	53808	52590	43510	30416
Experimental error	±11.7%	±11.2%	±13.1%	±13.5%
Na content (ppm)	109.3	111.5	73.7	52.3

	Sample number			
	O124–96C	O124–96S	O124–96H	O124–96B
Counts/h/g	125540	142037	97884	32264
	134199	139490	94250	31896
	127097	129971	101511	29385
	135427	130834	111688	31352
	122380	135147	110809	28522
	133391	122166	103590	31795
	122644	125917	107668	27652
	144761	123433	105420	27593
		129349		
Irradiation time	7 h 15 min	7 h 15 min	7 h 15 min	7 h 20 min
Counting time	10 min	10 min	10 min	10 min
$\bar{N}$	130680	130926	104103	30057
2σ	14374	12928	11394	3714
Relative error	±11.0%	±9.9%	±10.9%	±12.4%
Na content (ppm)	30.8	30.8	24.4	8.1

Table 2. Potassium in sidewinder propellant.

	Sample number			
	0124–96M	0124–96B	0124–96C	0124–96F
Counts/h/g	1823	890	2691	5482
	1736	811	2090	5836
	1970	717	2646	4577
			2798	
			2780	
Irradiation time	4 h 25 min	4 h 25 min	4 h 25 min	4 h 25 min
Counting time	40 min	40 min	40 min	40 min
$\overline{N}$	1843	806	2601	5298
2σ	194	142	522	1060
Experimental error	±10.5%	±17.6%	±20.0%	±20.0%
K content (ppm)	28.8	11.1	40.6	82.8

	Sample number			
	O124–96A	O124–96H	O124–96Q	O124–96S
Counts/h/g	2768	2524	2976	2036
	2266	2770	3320	2259
	2521	2956	3054	1649
Irradiation time	4 h 25 min	4 h 25 min	4 h 25 min	4 h 15 min
Counting time	40 min	40 min	40 min	40 min
$\overline{N}$	2518	2750	3116	1981
2σ	408	354	294	504
Experimental error	±16.2%	±12.9%	±±9.4%	±25.4%
K content (ppm)	39.3	43.0	48.7	32.0

there is a 95% probability that the actual values for potassium and sodium content are within the limits reported.

IV. Acknowledgments

The authors are grateful for the assistance rendered by Messrs. D. M. Shores and G. E. Holloway of the Naval Research Laboratory and Messrs. M. H. Rison and R. W. McKain of the Naval Ordnance Station in the preparation of this paper.

V. References

[1] Vogt, R. H., and Cosgrove, C. M., NRL Report 6704, April 18, 1968.
[2] Baumgartner, F., Table of Neutron Activation Constants, Verlag Karl Thiemig Kg, 1967.

THE APPLICATION OF ISOTOPIC NEUTRON SOURCES TO CHEMICAL ANALYSIS FOR PROCESS CONTROL IN THE METALLURGICAL INDUSTRY

J. Kuusi

Technical University of Helsinki
Reactor Laboratory
Otaniemi (Helsinki), Finland

I. Introduction

Isotopic neutron sources offer a simple and economical way to use neutron activation analysis in industrial process control. Potential applications have been discussed and feasibility studies have been described in several papers [1-6] but the routine use of sources remains limited.

This work describes laboratory measurements which were made during the development of an analyzer for determining silicon in ores, concentrates, charges, slags, *etc.* by fast neutron activation analysis using an ^{241}Am/Be neutron source. In some processes chromium, aluminum, and silicon can all be determined simultaneously.

A rapid method of monitoring silicon content is a general requirement for processing various metals. The determination of silicon, aluminum, and chromium by chemical methods is time consuming and laborious. X-ray analysis of silicon and aluminum content is complicated because characteristic x-rays of these elements are soft. The matrix effects are severe, and special methods of sample preparation are required [7-8].

Fast neutron activation analysis of silicon and aluminum content using neutron generators has been shown to be feasible and precise [9-11]. The high cost and bulk of neutron generators and the limited lifetime of the neutron producing tube or target are drawbacks in applications to industrial process control.

Small size, long life time and low cost are advantages of low intensity and long-lived isotopic neutron sources. The drawback of the low intensity can be overcome by using large samples. This can be done particularly well in the determination of silicon, aluminum, and chromium by fast neutron activation analysis, as the other elements generally present in the samples have small cross sections both for fast neutrons and for the gamma rays produced. Thus flux depression and matrix absorption effects are negligible even in samples of considerable volume.

The determination of silicon is based on the fact that the quantity of ^{28}Al ($T_{1/2}=2.3$ min) produced by activation with fast neutrons *via* the $^{28}Si(n,p)^{28}Al$ reaction is proportional to the quantity of silicon present in the sample. Counts accumulated under the 1.78 MeV photopeak are used as a measure of the extent of the reaction. Chromium is determined using counts accumulated under the 1.43 MeV photopeak of ^{52}V ($T_{1/2}=3.77$ min) produced *via* the $^{52}Cr(n,p)^{52}V$ reaction and aluminum using counts under the 0.84 and 1.01 MeV photopeaks of ^{27}Mg($T_{1/2}=9.5$ min) produced *via* the $^{27}Al(n,p)^{27}Mg$ reaction.

Phosphorus, aluminum, iron and manganese present in the sample can interfere with the determination of silicon. ^{28}Al can also be produced by activation with fast neutrons *via* the $^{31}P(n,\alpha)^{28}Al$ reaction and by activation with thermal neutrons *via* the $^{27}Al(n,\gamma)^{28}Al$ reaction. ^{56}Mn produced from ^{56}Fe by activation with fast neutrons and from ^{55}Mn by activation with thermal neutrons, emits gamma rays of energy of 0.84, 1.81 and 2.12 MeV. The 1.81 MeV photopeak interferes with the determination of silicon and the 0.84 MeV peak with the determination of aluminum. Vanadium present in the sample can interfere with the determination of chromium because ^{52}V is also produced *via* the $^{51}V(n,\gamma)^{52}V$ reaction by activation with fast and thermal neutrons.

II. Experimental

Irradiation and counting geometries are shown in Figure 1. The sample material having a volume of 480 cm³ was contained in a cylindrical plastic vessel having a cylindrical hole on the axis for the 3 Ci $^{241}Am/Be$ neutron

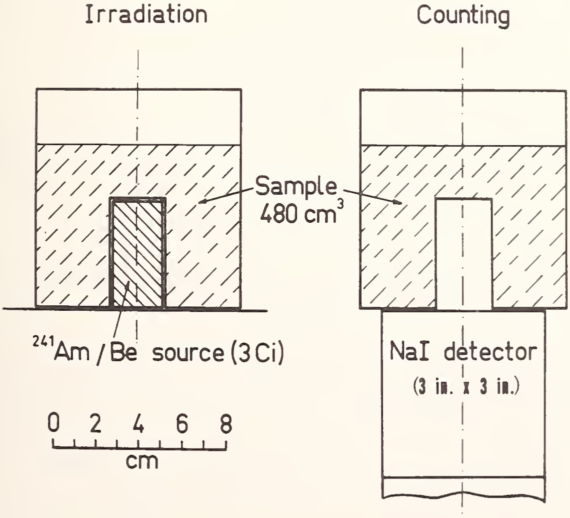


Figure 1. Irradiation and counting geometries.

source. After irradiation the vessel was placed on a 3 in. × 3 in. NaI detector for counting with a multichannel pulse-height analyzer. In the instrument to be constructed for industrial use the efficiency of the geometry will be improved substantially.

Irradiation and counting times of 10 min were used.

III. Results and Discussion

A. Results

Gamma spectra from irradiated chrome concentrate and pyrite smelter slag are shown in Figure 2. In the former, the contributions of ^{28}Al, ^{52}V and ^{27}Mg can be clearly seen. In the latter the ^{28}Al 1.78 MeV photopeak is dominant.

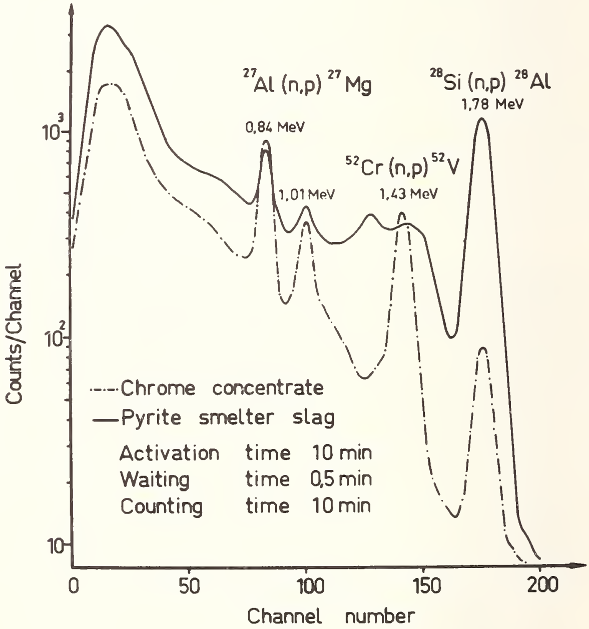


Figure 2. Gamma spectra from the activated chrome concentrate (1.6% Si, 30.2% Cr, 7.2% Al) and pyrite smelter slag (19.5% Si) samples.

Counts accumulated under the ^{28}Al 1.78 MeV photopeak plotted against the chemically determined silicon content of samples with large differences in the silicon content and matrix composition are shown in Figure 3. Throughout this work counts obtained with the fixed volume samples have been normalized to correspond to the samples of 1000 g of weight. The density of the same type of the samples was held constant.

No corrections for differences in absorption in the samples with different density have been made. The number of counts increases linearly with increasing silicon content and is thus fairly insensitive to large variations in the matrix composition. The statistical error of counting corresponds to an inaccuracy of ±0.06% Si when the silicon content is 2% and ±0.2% Si when this is 15%.

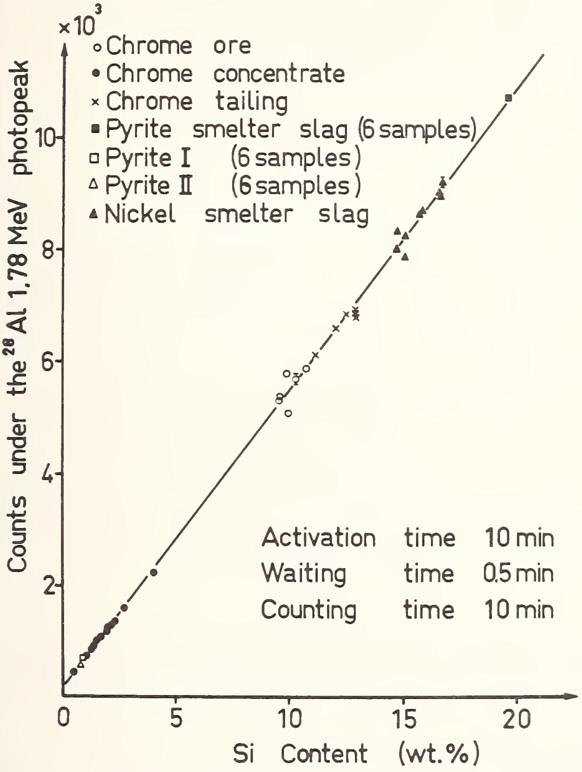


Figure 3. Counts accumulated under the ^{28}Al 1.78 MeV photopeak plotted against the chemically determined silicon content.

Counts accumulated under the ^{52}V 1.43 MeV photopeak plotted against the chemically determined chromium content of chrome ore, concentrate and tailing samples are shown in Figure 4. The contribution from the continuous part of the ^{28}Al spectrum to the chromium channel has been subtracted using counts in the silicon channel and a coefficient determined from the pure ^{28}Al spectrum. The effects of the differences in the density between the different types of the samples are becoming distinguishable. The points corresponding to the ore samples with the lowest density tend to lie above the calibration curve. The statistical error of counting corresponds to an inaccuracy of ± 0.75% Cr in the concentrates.

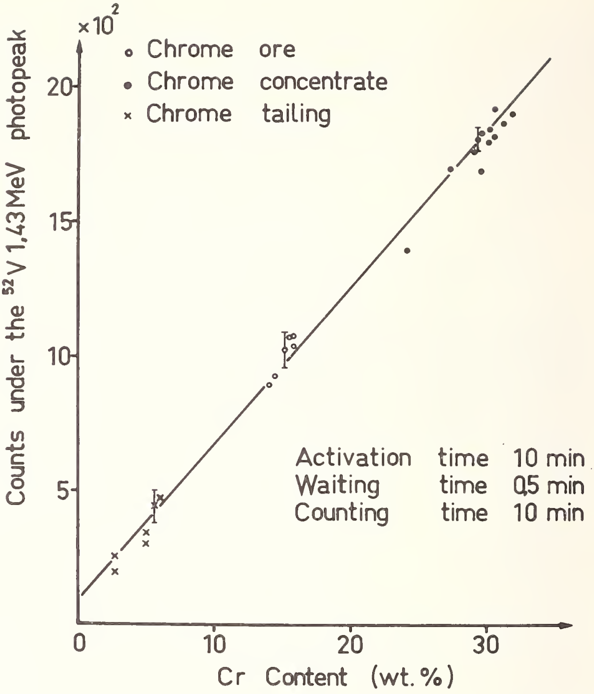


Figure 4. Counts accumulated under the ^{52}V, 1.43 MeV photopeak plotted against the chemically determined chromium content of chrome ore, concentrate and tailing samples.

Counts accumulated under the ^{27}Mg, 0.84 and 1.01 MeV photopeaks plotted against the chemically determined aluminum content of the chrome concentrate and ore samples are shown in Figure 5. Contributions from the continuous parts of the ^{28}Al and ^{52}V spectra to the aluminum channel have been subtracted. The effects of the difference in the density between the ore and concentrate samples are becoming clearer when the energies of the detected gamma rays are decreasing. It would be better to use separate calibration curves for different types of the samples. The statistical error of counting corresponds to an inaccuracy of ±0.13% Al in the concentrates.

B. Discussion

Of the applications described, the determination of silicon seems to be the most attractive. Because of the relatively short half life of ^{28}Al, activation and counting times shorter than 10 min may be used. With 10 min times, 90% of the saturation value of counts is reached, and with 5 min 61% is attained.

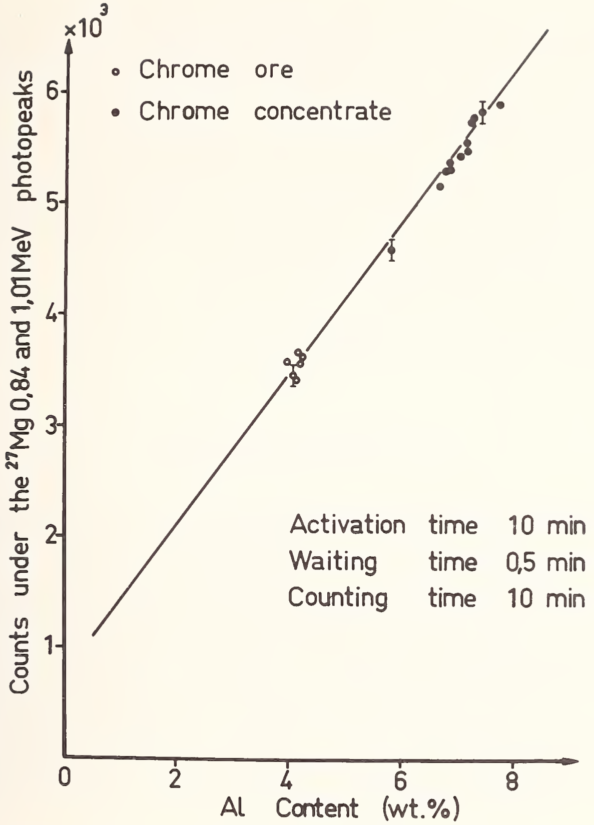


Figure 5. Counts accumulated under the ^{27}Mg, 0.84 and 1.01 MeV photopeaks plotted against the chemically determined aluminum content of the chrome ore and concentrate samples.

If optimum irradiation and counting geometries with several detectors are chosen, and a source of greater activity used; the number of counts accumulated can be made many times greater than in these preliminary measurements. Sufficient statistical accuracy can thus be attained for the accurate control of various processes.

The need for subtracting the contributions from other components in the counting channel makes the determination of chromium and aluminum more sensitive to interference than the determination of silicon. However, the accuracy of these determinations can be made sufficient for process control.

If shorter activation and counting times are used the reductions in counts accumulated are greater than in the case of silicon because of the longer half lives of ^{52}V and ^{27}Mg.

A particular advantage of the method using radioisotope source fast neutron activation analysis is that there is no need for sample preparation, thin detector windows or vacuum systems. Thus determinations may easily be made automatically. The amount of sample material required is large but usually this is available readily from metallurgical processes and there is no fear of matrix absorption effects when analyzing same types of the samples. When analyzing heterogeneous materials, large samples give reliable information on the average chemical composition. Pulverized, granulated or solid samples can be analyzed.

Standard nuclear instruments can be used in the analyzer. Thus it can be made into a reliable and relatively low cost device. The construction of prototypes for industrial use has commenced.

IV. Acknowledgments

The author is grateful to the management of the Outokumpu Central Laboratory in Pori, the Kokkola and Harjavalta Smelters and the Kemi chrome mine for provision of samples and chemical analyses without which this work could not have been accomplished. The development of the industrial instruments has been started in collaboration with the Outokumpu Research Laboratory in Tapiola. The author is indebted to Professor P. Jauho, Director of the Reactor Laboratory of the Technical University of Helsinki for his continued interest in this work. The economic support of The Finnish Atomic Energy Commission and of The Outokumpu Company is gratefully acknowledged.

V. References

[1] Anders, O. U., Nucleonics **20**, 78 (1962).
[2] Strain, J. E., and Lyon, W. S., in Radiochemical Methods of Analysis, Vol. I, I.A.E.A., Vienna, 1965, pp. 245-58.
[3] Christell, R., and Ljunggren, K., in Radiochemical Methods of Analysis, Vol. I, I.A.E.A., Vienna, 1965, pp. 263-74.
[4] Plaksin, I. N., Aleksandrov, Ch. A., and Starchik, L. P., in Activation Analysis, E. M. Lobanov, Ed., Acad. Sci. U.S.S.R., 1964, Engl. transl., Israel progr. sci. transl., Jerusalem, 1966.
[5] Beress, M., in Radioisotope Instruments in Industry and Geophysics, Vol. I, I.A.E.A., Vienna, 1966, pp. 365-80.
[6] Wing, J., and Wahlgren, M. A., Anal. Chem. **39**, 85 (1967).
[7] Uchida, K., Tominaga, H., and Inamura, H., in Radioisotope Instruments in Industry and Geophysics, Vol. I, I.A.E.A., Vienna, 1966, pp. 113-26.
[8] White, G., in Proceedings of the 19th Chemists' Conference, Scarborough, 1966, BISRA, London, 1966.
[9] Turner, S. E., Anal. Chem. **28**, 1457 (1956).
[10] Wing, J., Anal. Chem. **36**, 559 (1964).
[11] Vincent, H. A., and Volborth, A., Nuclear Applications **3**, 753 (1967).

ROUTINE DETERMINATION OF MAJOR COMPONENTS BY ACTIVATION ANALYSIS

James F. Cosgrove

The Bayside Laboratory
Research Center of General Telephone & Electronics Laboratories Incorporated
Bayside, New York

I. Introduction

The modern materials analysis laboratory requires a wide array of instrumentation and techniques to cope with all of the analytical problems with which it might be faced. An activation analysis facility employing an accelerator type neutron generator is a valuable adjunct to such an analytical laboratory. In our laboratory activation analysis has taken its place as a relatively comprehensive analytical system along with such techniques as x-ray, emission, mass, and atomic absorption spectroscopy and the more classical analytical methods. It has proven its worth in its ability to perform major component analyses nondestructively and much more rapidly than conventional methods with adequate accuracy and precision. A number of typical applications will be presented to exemplify the applicability of activation analysis as a routine technique for the determination of major components in a variety of samples.

II. Experimental

A. Apparatus

With a minimum of equipment, at a price that is by no means prohibitive, an activation analysis facility can be established which can effectively compete with other methods of elemental analysis for major components.

The neutron generator employed at our facility is a 200 kV TMC Model 211. It is equipped with a specially designed target holder capable of holding three targets. Each target can be conveniently rotated into the beam without disturbing the vacuum. The holder generally contains a fresh tritium target, a depleted tritium target and a deuterium target. The fresh target is used only when maximum sensitivity is required.

For macro analysis, short irradiations at low flux are usually sufficient to produce measurable activity from the elements of interest in the samples. Consequently a large number of irradiations can be performed before the target becomes useless. We can normally expect approximately 800 to 1000 irradiations per target.

A single sample pneumatic transfer system is utilized to transport the sample between the irradiation and counting stations.

The counting system consists of dual 3 in. × 3 in. sodium iodide crystals coupled to a 400 channel analyzer. Data readout is by means of an electric typewriter or punched paper tape.

B. Procedure

A purely instrumental approach is used. When radiochemical separations are required, the nondestructive nature of the technique is eliminated and the advantage of speed is lost. It is then usually more advantageous to resort to some other spectroscopic or chemical method of analysis. Samples and standards are irradiated sequentially and quantitative data are obtained from a comparison of the photopeak area. Irradiation and decay times are chosen to minimize interferences and depend on the particular sample.

III. Results and Discussion

When present in major concentrations almost all elements in the periodic table can be activated to a measurable extent using the 14 MeV, 3 MeV or thermal neutron capability of the generator.

The activation technique has found wide application in our laboratory for the determination of the composition of thin films. The development of methods for the preparation of thin films for surface passivation of semiconductor devices requires the concurrent development of analytical techniques capable of supplying information on the composition of such films. Activation analysis has been found to be an efficient method for the determination of the stoichiometry of thin films of silicon dioxide, aluminum oxide and mixed oxide films prepared by chemical vapor deposition. Conventional techniques require two samples to obtain the analytical data, one for the metal content and another for the oxygen content. These methods are, in addition, destructive. The activation technique permits the simultaneous determination of both elements and is nondestructive. Films weighing as little as 50 μg can be analyzed although the accuracy increases with sample weight as shown in Table 1. The results shown in the table were obtained on standard samples of aluminum oxide and silicon dioxide which had been weighed into sample capsules with a microbalance.

The electronic properties of some transition metal oxides notably those of vanadium and titanium, can be greatly affected by large lattice defects formed in certain of their monoxides. These oxides are good conductors, having resistivities similar to metals but in some cases with negative temperature coefficients. Both the resistivity and temperature coefficient of resistivity are strongly dependent on the oxygen-metal ratio. The correlation of resistivity measurements with metal and oxygen concentrations for simple and mixed oxides is essential in investigating the conduction mechanism. Fast neutron activation analysis is a rapid method for determining the oxide compositions. The total analysis time is approximately five minutes per sample. The precision is 3-5 relative percent at 95% confidence level.

These are but two examples of the use of activation analysis for the determination of major components. At the present time some thirty-five elements are determined in our laboratory on a routine basis in concentrations from 0.01% and higher in a variety of materials of interest to the electronics industry. The determination of activator and co-activator concentrations of phosphors, of the composition of alloys, glasses and frits can be readily carried out on the system. All of these analyses were formerly performed by standard spectroscopic or chemical methods. The use of activation analysis, where applicable, has considerably reduced the time required to obtain analytical data. Analytical time is measured in minutes rather than hours or days.

Table 1. Results of activation analysis of standard samples.

Sample	Sample wt (μg)	O/metal
SiO_2	40	1.28
SiO_2	88	1.11
SiO_2	220	1.15
SiO_2	558	1.14
SiO_2	926	1.14
Al_2O_3	85	0.77
Al_2O_3	292	0.89
Al_2O_3	464	0.87
Al_2O_3	798	0.89

Theoretical O/Si = 1.14
O/Al = 0.89

INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS USING REACTOR, Ge(Li) DETECTOR AND COMPUTER

Oswald U. Anders

The Dow Chemical Company
Radiochemistry Research Laboratory
Midland, Michigan

I. Introduction

The availability of a TRIGA reactor at The Dow Chemical Company made it possible to develop instrumental activation analysis into a general qualitative and quantitative analytical system capable of identifying up to ten elements simultaneously and providing quantitative assays from a single activation without chemical separations. The method is based on the following premises, the validity of which will have to be tested in detail by experience: The high resolution of the germanium detector makes it unnecessary to fit the peaks to a Gaussian curve for analysis; the relatively high gain stability of the spectrometer makes it unnecessary to gainshift the data and; composite peaks with unresolved maxima and two different half lives do not have to be considered specially, since they do not occur with sufficient frequency. It is sufficient to consider Compton continua in the region of a photopeak as a base upon which the photopeak is superimposed and to approximate the continuum by a straight line over the channels of the peak. The background as well as pulse-pileup distortions can be treated simultaneously with the Compton continuum except in regions where there are peaks in the background spectrum. The flux is known to about 1% standard deviation. The half lives of the isotopes giving gamma ray peaks are assumed to be known exactly from the literature or other sources.

II. Experimental

A. Apparatus

The 100 kW TRIGA reactor provides neutron fluxes of up to $1.6 \times 10^{12} n \cdot cm^{-2} \cdot sec^{-1}$ and has irradiation facilities in a rotary sample rack and a pneumatic tube system. Activations for the present work can be carried out in either facility.

The high resolution gamma-ray spectrometer consists of a 13 cm^3 coaxial lithium-drifted germanium diode mounted on a right angle dip stick cryostat with an ORTEC 118A preamplifier. It has a resolution for cobalt-60 gamma rays of 3.5 keV and a photopeak efficiency of 3% for 0.66 MeV gamma rays relative to a 3 in. diameter, 3 in. thick NaI detector and similar counting geometry. It is set up inside a lead cave with 2 in. thick walls. Samples are inserted into the counting position *via* a pneumatic sample changer system which can be timed electronically.

The gamma spectra are collected by a Nuclear Data 2200 system with 2048 channel memory and spectrum stabilizer. The output of the analyzer is by punched paper tape for computer use.

The Burroughs 5500 computer is used for analyzing the data and providing both the report of the analysis and a 10 cycle semilog plot of the normalized spectra of the samples.

B. Procedure

The procedure utilizes an arbitrary but fixed activation time. The samples are prepared in nitrogen atmosphere, packaged in 1/2 dram polyethylene vials and heat sealed. They are activated together with a flux monitor of potassium tartrate solution containing 10 mg potassium per ml.

After the activation the sample is transferred to the Ge(Li) detector and gamma spectra are collected at arbitrary times and for arbitrary counting periods. The output of a 60 cycle precision pulser is admixed to the signal from the detector at the preamplifier and produces a pulser peak falling between channel 2025 and channel 2048. This peak is used both for gain stabilization of the spectra and for the timing of the counting period. The latter was found to yield more reliable timing for high counting rates than using the live timer of the analyzer. It could be demonstrated that the peak distortion due to pulse pileup at high counting rates is identical for the photopeaks in the spectrum and for the pulser peak. Utilizing the peak area of the pulser peak for timing thus results in a correction for the pileup distortion in the peaks of interest and yields more reliable count rate data at high counting rates (~20,000 c/sec.). This expands the useful dynamic range of the counting system to accommodate activated samples initially rather strongly radioactive.

The flux value for the activation is obtained from the counts of the monitor as measured in a 3 in. well type NaI detector which has been calibrated using dilute gold solutions (0.1 mg/ml) activated in the reactor together with potassium-tartrate monitors.

C. Computer Program

The times of the activation, the flux to which the sample was exposed, the weight and volume of the sample as well as the beginnings and ends of the counting intervals, constitute the input data for the computer together with an arbitrary number of spectra of the sample.

The computer program, written in ALGOL language, first identifies the photopeaks in the spectrum, measures their energy equivalent and area, corrects the peak areas for the Compton-Bremsstrahlung-and background base of the peak, normalizes to counts per second and 1 × 10^{11}n·cm^{-2}·sec^{-1} flux. Due to the high resolution of the spectra and the good gain stability of the equipment, no peak fitting and gain shifting is necessary for processing [1]. The computer correlates the counting data for each peak energy as obtained at the different times, weights the data and calculates the half life for the peak by least squares technique. Using energy and half life the program identifies the element to which the peak belongs by comparison with a standards library. Using the "correct" half life information found in the library the computer now calculates the decay corrected "mean-time" of the counts for the particular gamma peak [2] and extrapolates the data to the end of the activation to obtain the normalized counting rate for the peak at that time. Comparison with the value for the count rate of the peak per mg of the element activated by the normal flux as contained in the library, yields the assay for the element as from that particular peak.

The program then sorts the results from individual gamma peaks by identified element and gamma energy and reports as output: the element identified, the gamma energies and half lives found in the spectrum as well as the corresponding ones reported in the library. It prints out the extrapolated normalized count rates of the identified peaks as well as the corresponding values for 1 mg as found in the library. All values are given with their respective error limits. The elemental content in mg as well as the concentration in the sample is then reported. Gamma energies not identified but present in the library for the identified elements are reported as "not found", to give an estimate of the validity of the results. A weighed average is then taken of the results obtained for the same element from the different gamma peaks and reported as the assay of the sample.

Finally the computer uses the amounts for each element found in the sample and calculates, with the aid of the self-shielding parameters for the identified elements as stored in the library, an estimate of the flux depression suffered by the sample during the activation. If this is significant (more than 1%) the computer puts out a warning to the experimenter. Computer processing time is on the order of 100 seconds.

If desired, the computer program can generate a semi-log plot of the normalized spectrum. It plots the identified peaks channel for channel and smoothes the regions between the identified peaks to maintain clarity of the graph. This plot is used by the experimenter to evaluate the validity of the results and search visually for peak patterns too small for the computer to recognize, generally stemming from trace impurities.

III. Results and Discussion

A. RESULTS

A set of specially prepared standard samples similar to the one used earlier for a similar purpose [3] has been processed for 5 minute activations in fluxes of approximately $1.5 \times 10^{12} n \cdot cm^{-2} \cdot sec^{-1}$ to obtain the data for the standards library of the program. A collection of the resulting elemental spectra indicates the presence of trace impurities in most of them (Fig. 1). The contributions of the latter are relatively small and readily identifiable. Information from their activation products was eliminated from the standards library content by inspection of the plots and evaluation of the digital results. A typical example of the results obtained for an "unknown" sample is presented in Table 1. Both the fact that the computer correctly identified the proper elements and completed the quantitative assay with reasonably small errors prove the validity of the premises for the method.

B. DISCUSSION

This work demonstrates the abilities of instrumental neutron activation analysis for qualitative as well as quantitative analysis of samples for elements present in concentrations between several present and a few parts per million. The combination of a nuclear reactor together with the high resolution gamma spectrometer and a power computer made it feasible.

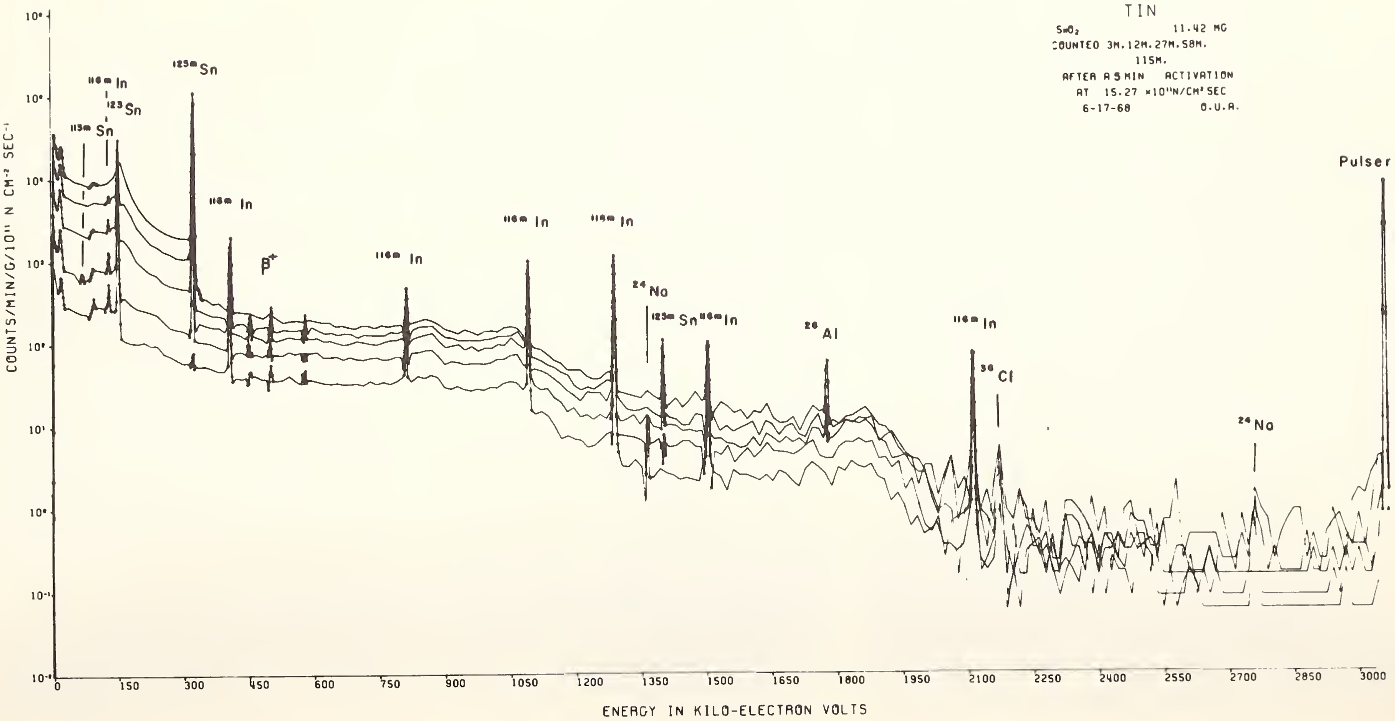


Figure 1. Spectrum of irradiated tin oxide standard.

Table 1. Results of the analysis of typical "unknown" samples processed by the computerized instrumental activation

Element:	P	Sn	K	Cl	Mg	Na
Weight (mg)						
present	53.3	2.80	44.1	2.35	6.53	1.627
found	55.9	2.78 2.80	44.38	2.37 2.39	6.93	1.626 1.69
Percent						
present	3.57	0.187	2.95	0.157	0.437	0.1099
found	3.74	0.186 0.187	2.97	0.158 0.160	0.464	0.1090 0.113
Isotope	^{28}Al	^{123m}Sn ^{125m}Sn	^{42}K	^{38}Cl	^{27}Mg	^{24}Na
Gamma-ray energy (keV)						
known	1779	161 331	1524	1642 2169	843	2757 1368
found	1781	161 331	1526	1644 2171	843	2760 1369
Half life	2.3 min	41 min 9.7 min	12.4 h	37.7 min	9.5 min	15.0 h
Counts $\cdot$ sec^{-1} $\cdot$ mg^{-1}						
per flux	0.150	1.139 20.12	0.0194	0.709 0.661	0.702	0.315 0.784

IV. References

[1] Helmer, R. G., Heath, R. L., *et al,* Linear Least Squares Fitting Program for the Analysis of Gamma Ray Spectra Including a Gainshift Routine, IDO-17015 (1964).

[2] Hoffman, W., and VanCamerik, S. B., Anal. Chem. **39,** 1198-9 (1967).

[3] Anders, O. U., and Beamer, W. H., Anal. Chem. **33,** 226-30 (1961).

CHAPTER 6

GENERAL APPLICATIONS

Synopsis of Discussions

DONALD E. WOOD, *Chairman*

Kaman Nuclear
Colorado Springs, Colorado

The title of General Applications indicates that a central theme is not available to unify the summary. Instead, I will review occasional features of the papers and the worthwhile points of discussion. Four out of the 17 papers were read since the authors were unable to attend; therefore, no discussion was available for these papers.

Merlini *et al.* discussed the analysis of freshwater microplankton. The calcium content was found to be independent of the calcium content of the four lakes from which samples were obtained. Concentration factors for Ca, Na, K, and Mn varied from 4 to 300, but the significance of these elements and their variation to the life cycle of the organisms is not yet known.

Papers by Mantel *et al.* and by Brownlee discussed measurement of the $^{235}U/^{238}U$ ratio by means of gamma-ray spectroscopy and delayed neutron analysis, respectively. These efforts are part of the basic work necessary to provide a useful system for the detection, inspection and assay of nuclear fuels at all stages of the fuel cycle (raw material, enrichment, fabrication, completed fuel elements, spent fuel, waste, and scrap). A major effort is needed to provide good inventory information, and activation analysis shows great promise in this area. Studies have not yet been extended to large samples of arbitrary geometry, but this should follow shortly after the basic work is completed.

Pulsed reactor work was reported by Naughton, and enhancement factors for short-lived isotopes were given. The pulsed method (10 msec pulses) is superior in sensitivity to steady-state activation for half lives below 20 msec. A special transfer system was designed to strip the rabbit from the sample before counting since ^{28}Al interference was troublesome. The problem of obtaining clean sample containers for trace analysis continues to annoy analysts.

The new facilities at Grenoble were described by Laverlochere. One of the machines is a high-yield Cockcroft-Walton accelerator, operating at 400 kV and 2 mA. Target half life was said to be 8 hours.

At the NRL cyclotron (Eisele) one of the applications is measurement of calcium isotopic variations by study of the ^{44}Ca/^{48}Ca ratio. During the discussion, ^{43}Ca was suggested as a better indication than ^{44}Ca, since its normal abundance is closer to that of ^{48}Ca.

The Siemens Research Laboratories reported work on localization of impurities in semiconductor silicon by Martin. Autoradiography was used to demonstrate that the impurities were not uniform; in fact, much of the impurity was concentrated at the edge of the zone of interest or at a few points of the interior. Thus, the desired semiconductor properties are only slightly affected instead of being severely affected as would have been expected from the average impurity concentration.

Ortega discussed activation analysis of laser crystals. This analysis is similar to the semiconductor problem in that position of impurities in the lattice structure is just as important as the total amount of impurity present.

The above 2 papers indicate a need for a new dimension (in fact, 3 dimensions) in activation analysis, since position needs to be determined. Work on the charged-particle equivalent of the electron microprobe is just getting underway and may lead to an expanded attack on the question of "where" is the material, in addition to our current questions of "what is it" and "how much". The use of a small collimated beam scanning the material combined with a mass spectrometer looks quite promising in this area.

The reactor program at Union Carbide (Nass) includes analysis of Se in blood. During the discussion, pretreatment to reduce interference was suggested to improve sensitivity. However this is not currently done because the sensitivity is already better than required.

SUBSTOICHIOMETRIC DETERMINATION OF MOLYBDENUM AND PALLADIUM BY NEUTRON ACTIVATION ANALYSIS

Z. K. Doctor, R. A. Nadkarni and B. C. Haldar

Inorganic and Nuclear Chemistry Laboratory
Institute of Science
Bombay-32, India

I. Introduction

The substoichiometric separation method substantially reduces the time for radiochemical procedure employed in activation analysis by eliminating the need for chemical yield determination. Stary *et al* [1] have described the substoichiometric determination of traces of molybdenum in GeO_2 by neutron activation analysis based on the extraction of molybdenum oxinate into chloroform. However, this method involves a cooling period of three days after irradiation and is not suitable for the estimation of small amounts of molybdenum in alloy steels, because large excess of iron interferes. The selective extraction of molybdenum (VI) into chloroform with α-benzoinoxime [2] permits its separation from other elements except tungsten with which it is commonly associated. In the present investigation use is made of the extraction of molybdenum α-benzoinoximate into chloroform to develop a simple and rapid method for the substoichiometric determination of small amounts of molybdenum in steel by thermal neutron activation.

Various investigators [3-6] have estimated traces of palladium in different matrices by neutron activation analysis but the substoichiometric procedure for palladium determination has not been reported. A method is described for the substoichimetric determination of microgram amounts of palladium by neutron activation method involving extraction of palladium with isonitrosoacetophenone (HINAP) [7].

II. Experimental

A. Apparatus and Reagents

A gamma-ray spectrometer provided with a single channel pulse-height analyzer and a well type 1.5 in. × 1.5 in. NaI(Tl) crystal detector, an end window type G.M. counter, and an aluminum absorber of thickness, 13.5 mg/cm^2.

MoO_3, Na_2MoO_4, and $PdCl_2$ of purity better than 99.9% were used as standards. Carriers were made by dissolving appropriate salts in water to give 10 mg of the element per ml of solution. α-benzoinoxime in twice distilled chloroform and HINAP in benzene were employed to extract molybdenum and palladium, respectively. Reagents and solvents used were of A.R. grade. Tracers were obtained from Isotope Division, Bhabha Atomic Research Centre, Trombay, India.

B. IRRADIATION

The samples of alloy steel (10-60 mg) in the form of fine turnings and standards of MoO_3 (1-4 mg) and Na_2MoO_3 (100 μg of Mo) were sealed in quartz ampoules and simultaneously irradiated for 4-68 hours in the Apsara Reactor of the Bhabha Atomic Research Centre, Trombay, at a thermal neutron flux of $1.5 - 2.0 \times 10^{12} n \cdot cm^{-2} \cdot sec^{-1}$. 5-15 mg of silver alloy and palladium comparators (0.005-10.0 μg of Pd) were irradiated for 2-24 hours.

III. Procedure

A. DETERMINATION OF MOLYBDENUM IN STEELS

The irradiated samples were weighed and dissolved in a mixture of 10 ml of conc. HCl, 2 ml of conc. HNO_3, 2 ml of bromine water and 10 mg of each of Mo(VI), W(VI), Ni(II), Mn(II), Si(IV), P(V) and S(VI) carriers. The solution was centrifuged to remove WO_3, made 6.5 N with respect to HCl and extracted twice with 20 ml of ethyl ether saturated with 6.5 N HCl. Molybdenum was re-extracted into the aqueous phase by equilibrating the combined ether extract twice with 5 ml of water. The aqueous phase was scavenged with benzidine tungstate, treated with 2 ml of 0.1 M Na_2(EDTA) and 2 drops of bromine, and made $0.6 - 0.8$ ~ with respect to HCl. The mixture was shaken for four minutes with 5 ml of 0.02 M chloroform solution of α-benzoinoxime. The organic phase was washed with 5 ml of 0.8 N HCl and evaporated to dryness. The activity of the residue was counted for 1-2 minutes on an end-window G.M. counter through 13.5 mg/cm^2 of aluminum absorber to eliminate counting of the conversion electrons of ^{99m}Tc. After allowing molybdenum activity to attain equilibrium with the daughter ^{99m}Tc, the sample was also counted on a gamma-ray spectrometer at the channel corresponding to the 0.147 MeV photopeak of ^{99}Mo. If tungsten is not present it is unnecessary to add tungsten carrier and scavenge solutions with WO_3 and benzidine tungstate. A simultaneously irradiated molybdenum standard was dissolved in dilute NaOH solution and the volume was made up to 100 ml with water. An aliquot (1-2 ml) of this solution was processed in exactly the same way as described above for the alloy steel.

B. DETERMINATION OF PALLADIUM IN SILVER ALLOY

A known amount of the irradiated sample was transferred into a 50-ml beaker and dissolved in minimum volume of 1:1 HNO_3 by heating the solution in the presence of 5.44 mg of Pd, 2 mg of Au and 1 mg of Os carriers. The solution was evaporated nearly to dryness with 0.4 ml of 6 *N* HCl. 2 ml of water were added and AgCl was removed by centrifugation. The supernatant was treated with 1 ml of 2% hydroquinone and 2 drops of silver nitrate solution. The precipitate was centrifuged. The supernatant was transferred to a 50-ml separatory funnel and made 1 *N* with respect to acetic acid keeping the total volume of the solution to 10 ml. It was then extracted with 10 ml of 0.0067 *M* solution of HINAP in benzene. The organic phase was centrifuged and 5 ml of the organic extract were counted on the gamma-ray spectrometer with 5 volts window and the channel setting of the analyzer corresponding to the minimum of the curve under the 0.087 MeV photopeak of ^{109}Pd. Samples were also measured on a G.M. counter after evaporating an aliquot of the organic extract in a counting dish. The standards were processed and counted as described above.

IV. Results and Discussion

A. RESULTS

Table 1. Substoichiometric determination of molybdenum by neutron activation analysis.

Duration of irradiation	Sample irradiated	Molybdenum Present	Molybdenum Found
7 days	Artificial mixture	46.96 ppm	47.74 ppm
"	"	375.7 ppm	384.7 ppm
"	"	469.6 ppm	462.0 ppm
"	10 mg of steel	0.43 %	0.423 %[a]
4 hrs to 7 days	16–60 mg of steel	"	0.425 ± 0.01%[b]

[a] Average of duplicate analysis.

[b] Average of eight determinations at 95% confidence limit.

Table 2. Substoichiometric determination of palladium by neutron activation analysis.

Duration of irradiation (hours)	Sample irradiated	Palladium in μ g Taken	Palladium in μ g Found
2 – 24	Artificial mixture	2.0	1.95 ± 0.06[a]
24	"	0.005	0.005
"	"	0.01	0.01
2	"	0.01	0.01
1 – 2	5 mg of silver alloy	5.0	5.0
	10 mg of silver alloy	10.0	10.4 ± 0.4[b]
	15 mg of silver alloy	15.0	15.4

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[a] An average of 4 determinations.

[b] An average of 4 determinations at 95% confidence limit.

B. Discussion

The artificial mixture containing Fe, Cr, Ni, Co, Mn and traces of P, S and Mo, and a standard alloy steel, 60B, supplied by Bureau of Analyzed Samples, England, were analyzed for Mo by the proposed method. The results are in good agreement with the reported value on the certificate of Bureau of Analyzed Samples. The accuracy and the precision of the method are 3.5% and 1.2% respectively. A statistical analysis of the results shows that with 16-60 mg of alloy-steel containing 0.43% Mo, the average value of eight determinations of molybdenum varies between 0.435% and 0.415% at 95% confidence limit. The sensitivity of the method is 0.2 μg of molybdenum. Two samples can be processed and counted on a G.M. counter within 30 minutes.

The method for Pd estimation was tested by analyzing a synthetic mixture containing 2.0 μg of Pd and 20-200 μg of each of Ru, Rh, Os, Ir, Pt, Ag and Au. With irradiation for two hours the procedure described above gives adequate decontamination of Pd from these elements. When samples are irradiated for 24 hours Au and Os activities are found to be present in the organic extract. Therefore, it is necessary to include an additional purification step which is as follows: After precipitation of Au and Os with hydroquinone, Pd is completely extracted with 0.047 M solution of HINAP in benzene and stripped from benzene extract by equilibration with 5 ml of 5 N HCl. The acid phase is treated with 3 ml of saturated solution of $Hg(NO_3)_2$, made 1 N with respect to acetic acid and extracted substoichiometrically by equilibration with 10 ml of 0.0067 M solution of HINAP in benzene. The results in Table 2 indicate that 2 μg of Pd can be determined with an accuracy of 4% and a precision of 3.7%. With 10 mg of silver alloy containing 3.89% Pt and 0.1% Pd, the average of four determinations of Pd is 10.4 μg which varies between 10.8 μg and 10.0 μg at 95% confidence limit. The time required for radiochemical purification and counting of the sample does not exceed 12 minutes. However, samples prepared by irradiating 0.005 μg of Pd for 24 hours require 20 minutes because they are counted for 10 minutes.

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V. References

[1] Stary, J., Ruzicka, J., and Zeeman, A., Anal. Chim. Acta **29,** 103 (1963).
[2] Knowles, H., Bur. Stds. J. Research **9,** 1 (1932).
[3] Brown, H., and Goldberg, E., U.S. Atomic Energy Commission, AECD-2296 (1948).
[4] Vincent, E. A., and Smales, A. A., Geochim. et Cosmochim Acta **9,** 154 (1956).
[5] Zvygintsev, D. E., and Kulak, A. I., Neorg. Khim. **2,** 1687 (1957).
[6] Killick, R. A., and Morris, D. F. C., Talanta **8,** 601 (1961).
[7] Talwar, U. B., and Haldar, B. C., Anal. Chim. Acta **39,** 264 (1967).

ACTIVATION ANALYSIS BY STANDARD ADDITION AND SOLVENT EXTRACTION. DETERMINATION OF CERTAIN TRACE ELEMENTS IN ANTIMONY

A. Alian

Nuclear Chemistry Department
Analytical Division
Atomic Energy Establishment
Cairo, U.A.R.

The high reproducibility of solvent extraction of trace amounts of metal ions from acidic solution has been utilized for developing a simple technique of activation analysis *e.g.* activation analysis by standard addition and solvent extraction [1,2]. In this technique the following variations in the experimental procedure could be adopted:

(1) A known amount of the sample and standard are irradiated under the same conditions and then completely dissolved.

(2) An aliquot of the sample solution is adjusted to the required conditions of extraction, the induced isotope is selectively separated by one or more extraction (or reextraction) steps and the activity of the extract measured.

(3) A suitable amount of the standard solution is added to another aliquot of the sample solution which is then adjusted to extraction; the induced isotope is separated and the activity of the extract measured under the same conditions of step 2. The amount of metal (x) to be determined is calculated from the equation:

$$x = x_s A/(A_m - A) \qquad (1)$$

where x = the amount of metal in the added standard solution, A and A_m are the activities (the photopeak activities in case of incomplete radiochemical purification) in two fractions recovered from the sample and from the mixture containing the same amount of sample and an amount of standard originally containing x_s of the element to be determined.

The advantage of this modification is simplicity and rapidity compared with the conventional method which would necessitate the separation of well defined precipitates suitable for weighing and counting. The technique was found to be suitable for the determination of elements such as uranium [2] and thorium [3] which on irradiation give rise to nuclides which have no stable isotopic carriers. In the simultaneous determination of many trace elements by this technique, the induced radioisotopes could be separated much more rapidly than by the usual method [4,6]. The technique has been also used for the rapid determination of traces of gallium [7] and antimony [8] in aluminum and rocks.

In the present communication the method is applied for the determination of traces of scandium, cobalt, thorium, zinc, silver and mercury in antimony. The induced ^{122} Sb and ^{124}Sb isotopes are separated by extraction with isopropyl ether, while the isotopes induced from the elements to be determined are fractionated by extraction with tridodecylamine, thenoyltrifluoroacetone and tributyl phosphate.

I. References

[1] Alian, A., Report A.E.E.T.-217, Bombay, India (1965).
[2] Alian, A., and Parthasarathy, R., Anal. Chim. Acta **35,** 69 (1966).
[3] Alian, A., and Sanard, W., Ibid **38,** 327 (1967).
[4] Alian, A., and Haggag, A., Talanta **14,** 1109 (1967).
[5] Alian, A., and Shabana, R., Michrochem. J. **12,** 426 (1967).
[6] Alian, A., and Shabana, R., Talanta **15,** 257 (1968).
[7] El-Sherif, A., Alian, A., Allam, B., and David, N., Radiochimica Acta **8,** 181 (1967).
[8] Alian, A., Shabana, R., Sanad, W., Allam, B., and Khalifa, H., Talanta **15,** 262 (1968).

NONDESTRUCTIVE DETERMINATION OF ELEMENTS IN SPECIFIC FRESHWATER MICROPLANKTON BY ACTIVATION ANALYSIS[1]

Margaret Merlini, Oscar Ravera and Carla Bigliocca

EURATOM Joint Research Center
Ispra, Italy

I. Introduction

Plankton composed of phytoplankton and zooplankton is a community of free-floating organisms living in marine and fresh waters. They are the first steps in the food chain in aquatic systems and as such, occupy a position of extreme importance. Elements, stable and/or radioactive are transferred from these first levels to successive trophic levels, and eventually some are incorporated into food items important to man. Thus, a knowledge of the chemical composition of plankton populations becomes essential, not only for an understanding of the passage of elements, beneficial and/or noxious through the food chain to man, but also for an understanding of the nutritional requirements of plankton with respect to the environment [1].

The first requirement for the study of microplankton is the separation, recovery, and accurate identification of the species. The amount of material obtained is in general small, and this limits the possibility of utilizing many known conventional chemical techniques. Since 1956 when Barnes [1] wrote that there was little or no bibliography on the elementary composition of freshwater microplankton, little has changed. There are, however, data for marine plankton *in toto* and for some species, especially macroplankton, done with modern techniques [2-6].

A seasonal study of the plankton populations of Lago Maggiore (Bay of Ispra) has been undertaken as part of a radioecological program for the study of the passage of stable and radionuclides through the food web [7]. Activation analysis provided the opportunity of determining the major elements Ca, Na, and K, as well as the trace element Mn, in samples of plankton of known composition in a relatively short time, and in a nondestructive fashion. Thus, the same samples will be used in the future for the determination of other elements.

This paper presents the method used in obtaining relatively pure samples of freshwater microplankton and the activation techniques applied for the determination of the elements in zooplankton and phytoplankton from Lago Maggiore. In addition, a comparison is made of the Ca content in 2 groups of zooplankton from 4 lakes: Lago Maggiore, Lago di Varese, Lago di Comabbio, and Lago di Monate.

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II. Experimental

A. MATERIALS AND METHODS (BIOLOGICAL)

Plankton samples were collected from different depths in each of the 4 lakes according to the maximum depth of the particular lake. All collections were made by vertical net hauls at about midday with a net 130 cm in length, 50 cm in diameter and with a pore size of 85 μm.

Each plankton sample of about 10 liters was divided into 3 subsamples and the volumes were measured. The first subsample was used for microscopic analysis, the second for pigment analysis, and the third for biomass evaluation and for elemental analyses. Each subsample was sieved gently through 6 "Eterlon" discs of different pore size to obtain organisms of similar dimensions. The fractions and sizes obtained were: I = >1180 μm; II = 950 μm to 1180 μm; III = 700 μm to 950 μm; IV = 500 μm to 700 μm; V = 295 μm to 500 μm; and VI = 85 μm to 295 μm. In this way, the fractions were composed of a few species of zooplankton and in some cases, of only one species. Phytoplankton was concentrated in the finest fraction, number VI, and almost all the zooplankton from I to V.

Each fraction, on a weighed "Eterlon" disc, was dried at 105 °C for 24 hours to obtain the dry weight, and the samples were stored in polyethylene containers. The water content was found to vary between 90% and 98%. Table 1 gives the classification of the principal organisms obtained by filtration and used in this study.

B. ANALYTICAL METHODS

Analyses were carried out by neutron activation and gamma spectrometry of the irradiated samples.

The quantitative determinations of Ca and Mn were done by measuring the photopeak at 3083 keV for ^{49}Ca and at 846 keV for ^{56}Mn on a 3 in. × 3 in. NaI(Tl) crystal immediately after irradiation. The half life of 8.8 min of ^{49}Ca necessitates counting the sample in the shortest time possible; therefore, only 2 samples and a standard were irradiated at a time. The dried biological samples (15-50 mg), sealed in polyethylene bags, were irradiated for 2 min at a flux of 1.6×10^{13}n·cm^{-2}·sec^{-1}, then removed from the rabbit and counted. Each sample was counted twice to check on the decay time of ^{49}Ca and ^{56}Mn.

Table 1. Classification of principal organisms in net plankton collected from 4 subalpine lakes of Northern Italy.

ZOOPLANKTON

Class/Order:	Crustacea/Cladocera	Crustacea/Copepoda
Species:	1) Filter–feeding plankters: *Daphnia hyalina* *Diaphanosoma brachyurum* 2) Predators: *Leptodora kindti* *Bythotrephes longimanus*	1) Omnivorous plankters for Lago Maggiore: *Cyclops abyssorum* *Mesocyclops luckarti* 2) Filter–feeding plankters: *Eudiaptomus vulgaris* *Mixodiaptomus laciniatus*

PHYTOPLANKTON

	Chrysophyta	*Cyanophyta*
Class/Order:	Bacillariophyceae/Pennales	Cyanophyceae/Oscillatoriales
Species:	1) Diatoms, unicellular algae *Tabellaria fenestrata* *Tabellaria flocculosa*	1) Blue–green algae *Oscillatoria rubescens*

Na and K were determined the following day using the photopeak at 1368 keV for ^{24}Na and 1524 keV for ^{42}K on a Ge(Li) detector with a volume of 47 cm^3. The use of the semiconductor was necessary because: (1) the photopeaks of these two isotopes interfere with each other if the sample is counted on the scintillation crystal; and (2) in this case calculation of the area by subtracting background by linear interpolation results in a loss of K [8].

It was not possible to analyze contemporaneously the 4 elements with one measurement on the detector due to the interference of radioisotopes with shorter half lives. Figure 1 shows the spectra of an irradiated sample of phytoplankton after a decay of 10 min (A), and 40 hours (B). The results obtained on punched tape were transferred to a magnetic tape and the calculations were done by the IBM computer 360/65.

C. INTERFERENCES DUE TO ^{37}S

One cannot *a priori* exclude interferences due to S in the determination of biological samples since the half lives and the gamma energy of ^{37}S and ^{49}Ca are very close. The gamma emission rates of the 3.1 MeV peak of ^{49}Ca and ^{37}S in our average experimental conditions (irradiation time 2 min, decay time 15 min), are respectively 1000 and 10.5 gamma per minute per μg of irradiated element. Since the quantity of Ca is generally

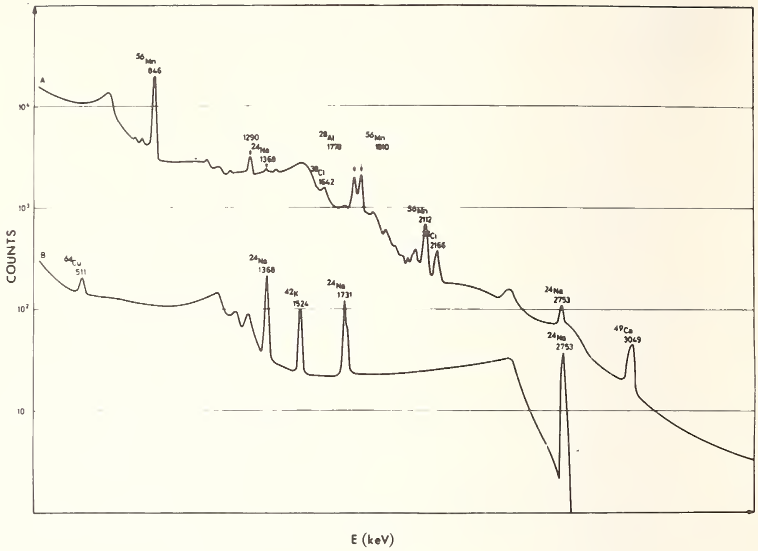

Figure 1. Spectra of an irradiated sample of phytoplankton (fraction VI) from Lago di Varese and counted on the Ge(Li) detector, after a decay of 10 min (A), and 40 h (B).

superior to 2000 parts per million (ppm), one can see that an hypothetical interference of 20,000 ppm of S would give an error of 10% in the determination of Ca, which is still reasonable for this method. Although very little is known about the S content of freshwater plankton, its concentration should not be higher than 3000 to 5000 ppm, based on data in the literature for phytoplankton [9,10]. The "apparent" Ca concentration due to the S content should not be higher than 30 to 50 ppm, which is well below the Ca values obtained. Qualitative analyses done with the Ge(Li) detector did not show any contribution of the ^{37}S peak.

III. Results and Discussion

Table 2 lists the results obtained for the quantities of Ca, Na, K, and Mn in different fractions of zooplankton and phytoplankton of Lago Maggiore. The number of samples examined was not the same because the quantity of zooplankton obtained at each collection was not always sufficient for analysis. Instead, phytoplankton was always abundant and it is interesting that the quantities of all the elements showed the greatest variation in this fraction. This is due, perhaps, to the seasonal changes in the structure and physiology of the biocenosis as pointed out by Ravera [11]. Also, of the 4 elements determined, the greatest variation was found for the K values in all groups.

Table 2. The concentration of calcium, sodium, potassium, and manganese in pure samples of microplankton from Lago Maggiore (Bay of Ispra).[a]

Sample	Fraction No.	No. of samples	μg element/g organism dry weight			
			Calcium	Sodium	Potassium	Manganese
Copepoda (large)	IV	3	1603 ± 278	2200 ± 305	6450 ± 1688	18 ± 1.00
Copepoda (small)	V	6	1760 ± 238	1627 ± 143	8980 ± 2095	29 ± 1.53
Cladocera	III	3	60,000 ± 4163	543 ± 74	3567 ± 1718	46 ± 1.91
Phytoplankton	VI	11	1790 ± 234	209 ± 51	4433 ± 1456	72 ± 11.33

[a] The mean values and standard deviation of the mean are reported for μg element/g organism, dry weight (105°).

Since the silica content of diatoms (phytoplankton) is known to be high [12], the results have been calculated as mg element/Mg N_2 to avoid erroneous biological interpretations (Table 3). On this basis, it is clear that phytoplankton have more Ca than the Copepoda, more K and Mn than both zooplankton groups; and for the phytoplankton, the quantity of K is much higher than that of sodium. Calcium and potassium ions, rather than Na, are essential for the growth of green plants, thus, the higher levels of Ca and K than Na are in keeping with this fact.

Table 3. Abundance of stable calcium, sodium, potassium, and manganese in samples of microplankton from Lago Maggiore (Bay of Ispra).[a]

Sample	Fraction No.	mg Ca/mg N_2	mg Na/mg N_2	mg K/mg N_2	mg Mn/mg N_2
Cladocera	III	0.628	0.006	0.037	0.0005
Copepoda	V	0.020	0.018	0.101	0.0003
Phytoplankton	VI	0.075	0.009	0.185	0.0030

[a] The mean values are given as mg element/mg of N_2, dry weight.

It is maintained that surface binding is a major factor for the concentration of transition metals in the biosphere [13]. Phytoplankton provide a large surface area with respect to protoplasmic volume, and this may account for the high level of Mn observed since only small quantities of the element are required for autotrophic growth and for a specific photosynthetic function [14].

Of the 2 groups of zooplankton, the cladocerans contained significantly more Ca than the copepods. Fraction 3 was composed primarily of *Daphnia* and certain species of this genus are known to have higher levels of Ca than other Cladocera [9,15]. In addition, the heavier cuticle and frequent molting of these animals might induce a greater concentration of the element. Marshall and coworkers [15] have reported an average of 6.7 μg of Ca (about 0.81% wet weight) for the first instar adult of *Daphnia magna*.

Freshwater crustaceans, like all freshwater animals, have the problem of active absorption of ions from a dilute medium to replace those lost through excretion or outward diffusion [16]. Since few data exist concerning the ionic composition of the species studied, little can be said about the values given for Na and K.

Concentration factors (C.F.) calculated for the 4 elements in the 2 groups of zooplankton from Lago Maggiore gave the following results:

$$\text{Concentration factor} = \frac{\mu\text{g element/g wet wt animal}}{\mu\text{g element/ml lake water}}$$

Organism	Calcium	Sodium	Potassium	Manganese
Cladocera	180	18	119	138
Copepoda	4	54	300	87

Whatever the regulatory mechanism involved for Ca and Mn accumulation, it does not appear to be the same for the 2 groups of Crustacea. Perhaps the feeding habits and physiological involvements among the species investigated account for some of the differences observed. These factors have been shown to be important in the uptake of fission products by marine organisms including plankton as reported by Berner, *et al* [17].

Calcium was determined for the 2 groups of zooplankton from 4 limnologically different lake types, containing varying amounts of Ca in the water (Table 4). When the samples were composed of 95% to 100% Cladocera, the concentration factor for Ca was over 100. Copepoda, on the other hand, did not exceed 13. It is apparent that the concentration of the element is independent of the quantity of Ca found in the environment, indicating perhaps, a strict physiological control.

The results presented in the preliminary study of the elementary chemical composition of microplankton from lakes of Northern Italy have shown: (1) It is possible to determine Na, Ca, K, and Mn in a short time in small quantities of microplankton; the same samples can be used for the determination of other elements; (2) Relatively pure samples of freshwater microplankton were obtained by selective filtration. Results reported for phytoplankton and zooplankton help fill the gap in our knowledge of the amounts of major elements like Ca, Na, and K, as well as the trace element Mn, in these groups; (3) Phytoplankton (primarily *Tabellaria*) had higher levels of the required elements Ca and K than Na; (4) The Caldocera and Copepoda concentrate Ca by approximately the

Table 4. Concentration factors for calcium in Cladocera and Copepoda from 4 limnologically different lake types of Northern Italy.[a]

Lago di Varese, H_2O = 40 ppm Ca				Lago di Comabbio, H_2O = 25.5 ppm Ca			
% Cladocera	% Copepoda	μg Ca/g wet wt	C.F.[a]	% Cladocera	% Copepoda	μg Ca/g wet wt	C.F.[a]
--	--	--	--	0	100	84	3.3
97	1	4126	103	96	0	3277	128
Lago Maggiore, H_2O = 20 ppm				Lago di Monate, H_2O = 10 ppm			
0	100	81	4	3	87	132	13
100	0	3614	180	100	0	1325	132

$$^{a}\text{C.F.} = \frac{\mu\text{g element/g wet wt animal}}{\mu\text{g element/ml lake water}}$$

same factor (over 100 for Cladocera, less than 13 for Copepoda) irrespective of the Ca content in the water of the different lakes from which they were collected.

IV. References

[1] Barnes, H., Mem. Ist. Ital. Idrobiol. **9**, 113 (1956).

[2] Bielig, H. J., Schmidt, H. L., Rohns, G., and Klinger, Euratom Report 2771.d, 1966.

[3] Thompson, G., Bowen, V. T., Curl, H., Jr., and Nicholls, G. D., Report NYO-2174-60, 10 May 1967.

[4] Patten, B. C., Lowman, F. G., and Neal, E. C., Health Physics Division Annual Report for July 31, 1966. No. 170, ORNL Report 4007, pp. 93-98.

[5] Nicholls, G. D., Curl, H., Jr., and Bowen, V. T., Limnol. and Oceanogr. IV (4), 472 (1959).

[6] Ketchum, B. H., Bowen, V. T., and Ryther, J. H., Woods Hole Oceanogr. Inst. Ref. 57-18 (1957).

[7] Merlini, M., Girardi, F., and Pozzi, G., in Nuclear Activation Techniques in the Life Sciences, Intl. Atomic Energy Agency, Vienna, 1967, pp. 615-629.

[8] Girardi, F., Guzzi, G., and Pauly, J., Sonderdruck aus Radiochim. Acta **7**, 202 (1967).

[9] Vinogradov, A. P., The Elementary Chemical Composition of Marine Organisms, Sears Foundation Mar. Res., Memoir **2**, 1953.

[10] Bowen, H. J. M., Trace Elements in Biochemistry, Academic Press, London and New York, 1966.

[11] Ravera, O., Proc. of Intl. Limnol. Assoc. for 1968 (to be published).

[12] Hutchinson, G. E., A Treatise on Limnology, Vol. I, John Wiley and Sons, Inc., New York, 1957.

[13] Lowman, F. G., Report UWFL-54, USAEC, TID, Oak Ridge, Tenn., 1958.

[14] Tanner, H. A., Brown, T. E., Eyster, C., and Treharne, R. W., The Ohio Jour. of Science **60** (4), 231 (1960).

[15] Marshall, J. S., Beeton, A. M., Chandler, D. C., Verh. Internat. Verein. Limnol. XV, 665 (1964).

[16] Robertson, J. D., in the Physiology of Crustacea, Vol. I, T. H. Waterman, Ed., Academic Press, New York and London, 1960, pp. 317-339.

[17] Berner, L., Jr., Bieri, R., Goldberg, E. D., Martin, D., and Wisner, R. L., Limol. and Oceanogr. Supplement Vol. **7**, LXXXII (1962).

ISOTOPIC ANALYSIS OF URANIUM BY NEUTRON ACTIVATION AND HIGH RESOLUTION GAMMA-RAY SPECTROMETRY

M. Mantel, J. Gilat and S. Amiel

Soreq Nuclear Research Centre
Yavne, Israel

I. Introduction

In nuclear laboratories there is often need for a quick analysis (usually to a precision of 1%) of the isotopic composition of uranium samples to be used as target materials. The errors associated with conventional activation analysis (radiochemical separation of ^{239}Np and one or more fission products) are in the range 2-10% [1,2]. Neutron activation followed by counting of delayed neutrons involves errors of only about 0.5% [3]; however, the detector system must be placed near the pneumatic tube of a reactor. A simple and accurate method utilizing equipment normally found in nuclear laboratories will be described here.

With the advent of Ge(Li) detectors [4], high resolution gamma-ray spectrometry became feasible permitting simultaneous determination of a substantial number of separate gamma-ray peaks belonging to different species present in one sample. A case in point is the determination of isotopic ratios of elements, whenever two or more of the isotopes lead upon radioactivation to well identifiable species. By determination of these species in a single measurement (*i.e.*, a single gamma-ray spectrum) many of the common sources of error (flux variations, self-shielding, sample weight, chemical yield, counting geometry, *etc*.) cancel out and high precision that depends only on counting statistics and peak integration errors, is attainable.

Based on this principle the ratio ^{238}U/^{235}U in an uranium sample may be determined from the ratio of the peak intensities of ^{239}Np formed from ^{238}U by activation and those of fission products formed from ^{235}U. Several ^{239}Np peaks, as well as those of a number of fission products can easily be distinguished. Each spectrum yields, therefore, more than one peak ratio and the precision can be increased by averaging over several such ratios.

II. Experimental

A. Apparatus

A ~15 cm^3 Ge(Li) detector (5-side drifted to a depth of ~5 mm) was used. The output signals were passed into an Ortec model 118A preamplifier and an Ortec model 410 linear amplifier. The resultant pulses were analyzed by a 400 channel analyzer. The resolution of the system for the 122 keV and 1333 keV gamma rays of ^{57}Co and ^{60}Co was approximately 3.0 keV and 4.2 keV (FWHM), respectively.

B. Procedure

20-25 mg of the uranium sample were weighed into a small polyethylene bag, sealed, introduced into a polyethylene vial and irradiated for 5 minutes in the pneumatic tube of the IRR-1 reactor at a neutron flux of 4×10^{12} $n \cdot cm^{-2} \cdot sec^{-1}$. After a delay period of about 24 hours the sample was counted for at least 40 minutes. The peak intensities were calculated by subtraction of the background and the Compton contribution of higher energy peaks from the integrated number of counts under every characteristic photopeak following a procedure proposed by Guzzi *et al* [5]. After correction for decay the ratios between the integrated areas of 3 different photopeaks of ^{239}Np (105, 278 and 210 keV) and 6 different fission products: 67 h ^{99}Mo-6.0 h ^{99m}Tc, 140 keV; 33 h ^{143}Ce, 290 keV; 20.8 h ^{133}I, 530 keV; 9.7 h ^{91}Sr-51 min ^{91m}Y, 556 keV; 17 h ^{97}Zr-73 min ^{97}Nb, 6584 keV and 743 keV; 78 h ^{132}Te-2.3 h ^{132}I, 773 keV) were calculated and the $^{238}U/^{235}U$ ratio was determined from calibration curves which were constructed as follows:

Eight samples of U_3O_8 of known isotopic composition certified by the U.S. National Bureau of Standards containing different $^{238}U/^{235}U$ ratios were prepared, irradiated and counted as described above. The intensity ratios of the three ^{239}Np photopeaks and the seven fission product peaks, respectively, were plotted against the $^{238}U/^{235}U$ ratio of the samples. Straight lines of zero intercept were obtained in all cases. Figure 1 shows the lines obtained for some ^{239}Np/fission product ratios.

III. Results and Discussion

A. Results

A sample of natural uranium NBS Standard Reference Material No. 950 was analyzed as described above and the results compared with those obtained by neutron activation followed by counting of delayed neutrons. In this range of isotopic composition it is possible to neglect the

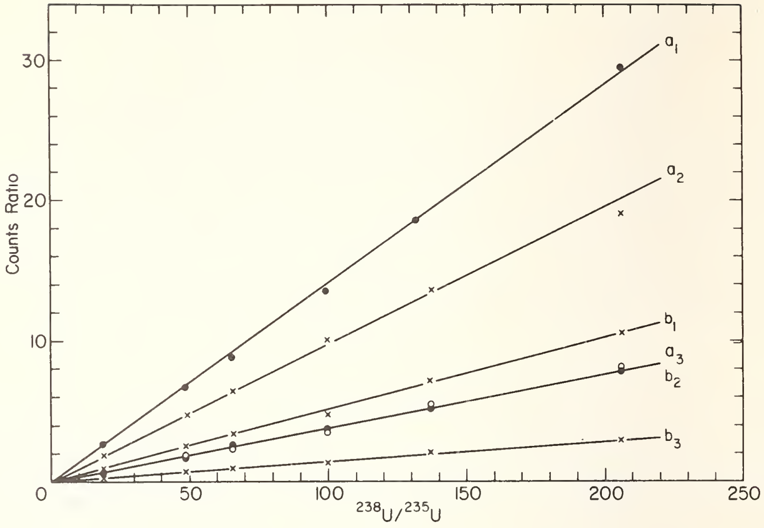

Figure 1. Activity ratios ^{239}Np/f.p. as a function of ^{238}U/^{235}U. $a_1 = {}^{239}$Np 105 keV/^{99}Mo; $a_2 = {}^{239}$NP 278 keV/^{99}Mo (x10); $a_3 = {}^{239}$Np 210 keV/^{99}Mo (x10); $b_1 = {}^{239}$Np 105 keV/^{133}I (x10^{-1}); $b_2 = {}^{239}$Np 278 keV/^{133}I; $b_3 = {}^{239}$Np 210 keV/^{133}I.

contribution of ^{234}U (about 0.005%) and directly compare the results of the two methods. Very good agreement for the ^{235}U content was obtained between the two methods – 0.718% ± 0.004 by delayed neutron counting vs. 0.720% ± 0.004 by the present method (using 0.720% ± 0.0007 [6] as standard value). The results obtained are shown in Table 1. Using all intensity ratios of 21 gamma-ray peaks, a precision of about ± 0.6% is obtained for a single determination. It is obvious that the precision of the method can be further increased in increasing the number of determinations.

Table 1. ^{238}U/^{235}U ratios derived from ^{239}Np/fission products analysis of NBS Standard Reference Material 950 (0.72% ^{235}U).

		^{97}Nb 658 keV	^{99}Mo	^{143}Ce	^{91}Y	^{133}I	^{132}I	^{97}Nb 743 keV
Np peaks relative to 278 keV \ fission products peaks relative to ^{97}Nb 658 keV		1	6.68 ± 0.2	1.32 ± 0.05	0.56 ± 0.01	1.76 ± 0.02	0.278 ± 0.007	1.02 ± 0.03
^{239}Np 278 keV	1	140	137	143	137	138	145	137
^{239}Np 105 keV	13.84 ± 0.32	138	138	135	144	133	138	146
^{239}Np 210 keV	0.391 ± 0.007	136	137	139	140	137	137	143

r = ^{238}U/^{235}U

m = mean value ^{238}U/^{235}U = 138.9

n = number of determinations

Standard deviation of single ratio $\left(\sqrt{\frac{\Sigma(r-m)^2}{n-1}} \cdot 100/m\right) = (2.6\%)$

mean standard deviation of all 21 ratios $\left(\sqrt{\frac{\Sigma(r-m)^2}{n(n-1)}} \quad 100/m\right) = (0.6\%)$

B. Discussion

Figure 2 shows some gamma-ray spectra obtained for NBS Standard Reference Materials with increasing ^{235}U concentrations (0.72, 2.10,

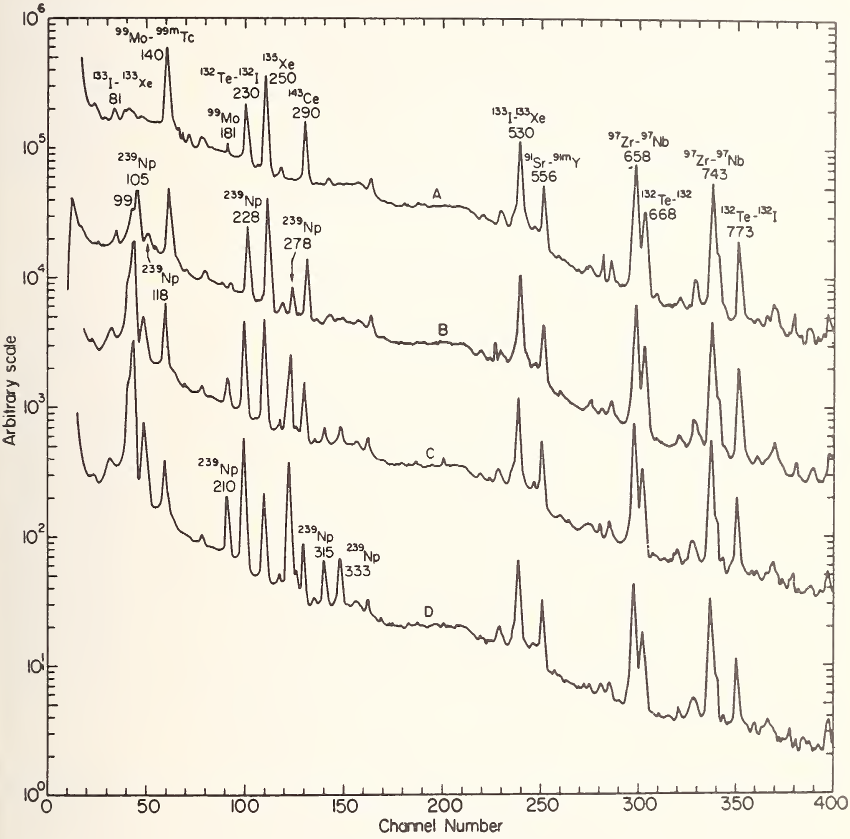

Figure 2. Gamma-ray spectra of NBS Standard Reference Materials with increasing ^{235}U content. A = 5 mg U_3O_8 93.27% ^{235}U 1 min irrad 24 h AEB 40 min count; B = 20 mg U_3O_8 10.007% ^{235}U 5 min irrad 24 h AEB 40 min count; C = 20 mg U_3O_8 2.10% ^{235}U 5 min irrad 24 h AEB 40 min count; D = 20 mg U_3O_8 0.72% ^{235}U 5 min irrad 24 h AEB 40 min count.

10.007 and 93.27% respectively) in the energy range from 0-800 keV, 24 hours after irradiation. For ^{235}U concentrations greater than 10%, the ^{239}Np peaks are almost completely masked by the much more prominent fission product activities. It is clear, therefore, that the technique as presented here is applicable only to low and intermediate ^{235}U concentrations, *viz* 10%.

A cooling period of 24 hours was chosen since by then the short-lived isotopes (^{91}Sr) will not have completely decayed, ^{99}Mo, ^{97}Zr and ^{132}Te will already be in equilibrium with their respective daughters and ^{239}U will have decayed to ^{239}Np.

In order to investigate the influence of Compton scattered higher energy gamma rays from fission products on the ^{239}Np photopeaks, pure neptunium was prepared by solvent extraction [7] from an irradiated natural U(0.72% ^{235}U) sample. The ratios of the principal ^{239}Np photopeak areas were calculated and compared with those obtained from the U_3O_8 samples with different ^{235}U contents. Results are summarized in Table 2. Based on these results, the photopeaks at 105, 210 and 278 keV were chosen as representative of the amount of ^{235}U in the samples.

Table 2. Ratio of ^{239}Np photopeak areas.

Sample	105/278 keV	105/210 keV	118/278 keV	210/278 keV	228/278 keV
^{239}Np[a]	13.95 ± 0.23[b]	35.11 ± 1.34[b]	2.19 ± 0.04[b]	0.40 ± 0.02[b]	1.15 ± 0.02[b]
^{235}U= 0.48%	13.30 ± 0.05	36.02 ± 0.31	1.50 ± 0.009	0.395 ± 0.003	1.262 ± 0.006
^{235}U= 0.72%	13.54 ± 0.06	36.01 ± 0.37	1.66 ± 0.01	0.382 ± 0.004	1.404 ± 0.006
^{235}U= 0.99%	14.03 ± 0.06	35.99 ± 0.39	1.80 ± 0.01	0.389 ± 0.005	1.608 ± 0.009
^{235}U= 1.51%	13.84 ± 0.07	35.00 ± 0.51	1.59 ± 0.01	0.388 ± 0.006	1.89 ± 0.01
^{235}U= 2.01%	14.12 ± 0.04	35.90 ± 0.75	1.65 ± 0.01	0.380 ± 0.008	1.914 ± 0.009
^{235}U= 4.95%	14.14 ± 0.25	34.89 ± 1.72	1.52 ± 0.04	0.40 ± 0.02	2.78 ± 0.05
^{235}U=10.007%	16.84 ± 0.15	45.08 ± 3.38	1.36 ± 0.05	0.40 ± 0.03	5.34 ± 0.06
Average[c]	13.84	35.56	1.70	0.391	[d]
Std. dev.	2.3%	± 1.48%	14.0%	1.8%	

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[a] Extracted with 0.5 *M* TTA (2–thenoyl–trifluoroacetone) – xylene [7] from an irradiated U_3O_8 NBS Standard Reference Material 950, natural uranium composition (0.72% ^{235}U).

[b] The error limits given are one standard deviation due to counting statistics only.

[c] Calculated for concentrations of ^{235}U up to 5%

[d] Average value not calculated, in view of the clear systematic trend in the data.

The ratios of the photopeaks of the principal fission products detected to the ^{97}Nb, 658 keV were calculated for samples of different ^{235}U content and compared with those obtained from a sample containing a high amount of ^{235}U(93.27%) in which ^{239}Np can be practically neglected. The results obtained are summarized in Table 3. No systematic variation of the ratios with the ^{235}U content can be seen. The variance of all ratios is compatible with that expected from counting statistics alone except for

Table 3. Photopeak areas of fission product relative to the ^{97}Nb 658 keV peak.

Sample ^{235}U%	^{99}Mo 140 keV	^{135}Xe 250 keV	^{143}Ce 290 keV	^{91}Y 556 keV	^{133}I 530 keV	^{132}I 668 keV	^{132}I 773 keV	^{97}Nb 743 keV
0.48	6.28 ± 0.13[a]	6.88 ± 0.12	1.23 ± 0.03	0.57 ± 0.02	1.77 ± 0.04	0.31 ± 0.01	0.27 ± 0.01	1.01 ± 0.02
0.72	6.54 ± 0.10	6.38 ± 0.11	1.34 ± 0.03	0.57 ± 0.02	1.77 ± 0.04	0.28 ± 0.01	0.28 ± 0.01	1.02 ± 0.02
0.99	6.36 ± 0.09	7.17 ± 0.11	1.29 ± 0.02	0.56 ± 0.01	1.78 ± 0.03	0.31 ± 0.001	0.280 ± 0.009	1.02 ± 0.02
1.51	6.61 ± 0.07	6.84 ± 0.07	1.36 ± 0.02	0.57 ± 0.01	1.77 ± 0.02	0.313 ± 0.009	0.282 ± 0.007	1.06 ± 0.02
2.01	6.75 ± 0.09	6.35 ± 0.08	1.36 ± 0.02	0.56 ± 0.01	1.75 ± 0.03	0.269 ± 0.009	0.27 ± 0.008	1.05 ± 0.01
4.95	6.53 ± 0.09	6.37 ± 0.09	1.36 ± 0.03	0.54 ± 0.02	1.73 ± 0.03	0.23 ± 0.01	0.281 ± 0.008	0.97 ± 0.02
10.007	6.90 ± 0.08	7.01 ± 0.06	1.38 ± 0.02	0.56 ± 0.01	1.78 ± 0.02	0.27 ± 0.008	0.29 ± 0.07	1.02 ± 0.01
93.27	7.08 ± 0.12	6.43 ± 0.06	1.39 ± 0.03	0.56 ± 0.01	1.75 ± 0.03	0.302 ± 0.006	0.272 ± 0.009	1.05 ± 0.02
Average	6.68	6.68	1.34	0.56	1.76	0.285	0.278	1.02
Std. dev. %	±3.4	±5.0	±3.9	±1.7	±1.0	±10.5	±2.6	±3.1

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[a] Error margins are one standard deviation due to counting statistics only.

^{132}I, 664 keV and ^{135}Xe, 250 keV. All the other 6 fission products were chosen as representative of the amount of ^{235}U in the sample.

To analyze the sources of error, we use the relation R_jF = constant, independent of F (R_j denotes a ^{239}Np/f.p. gamma-peak ratio, and $F = {}^{235}\text{U}/{}^{238}\text{U}$). For each ratio R_j, the product R_jF, averaged over all values of F is, as expected equal to the slope of the R_j vs. $1/F$ line, as determined by least squares analysis. Table 4 gives the values of the products determined by the two methods together with their respective standard deviations. A comparison of the average error expected from counting

Table 4. Analysis of errors.

		R_jF^a (× 10^2)	R_jFa^b (× 10^2)	Average standard deviation calculated from R_jF products (%)	Average error due to counting statistics (%)
^{239}Np 105 keV	^{99}Mo 140 keV	13.7	14.0	± 3.0	± 1.1
relative to:	^{143}Ce 190 keV	67.96	68.6	± 1.4	± 1.7
	^{91}Y 556 keV	154	154	± 1.6	± 2.2
	^{133}I 530 keV	50.5	51.1	± 2.1	± 1.2
	^{132}I 773 keV	328	329	± 0.6	± 3.0
	^{97}Nb 658 keV	90.6	90.5	± 1.9	± 1.5
	^{97}Nb 743 keV	87.0	87.2	± 2.6	± 1.5
^{239}Np 278 keV	^{99}Mo 140 keV	0.96	0.95	± 2.5	± 1.1
relative to:	^{143}Ce 290 keV	5.10	5.44	± 3.2	± 2.0
	^{91}Y 556 keV	11.6	11.7	± 2.4	± 2.6
	^{133}I 530 keV	3.93	3.98	± 3.2	± 1.4
	^{132}I 773 keV	24.8	25.3	± 2.8	± 3.1
	^{97}Nb 658 keV	6.66	6.92	± 3.4	± 1.9
	^{97}Nb 743 keV	6.79	6.80	± 1.6	± 3.8
^{239}Np 210 keV	^{99}Mo 140 keV	0.37	0.38	± 3.1	± 2.3
relative to:	^{143}Ce 290 keV	1.84	1.80	± 2.3	± 2.7
	^{91}Y 556 keV	4.30	4.23	± 3.6	± 3.3
	^{133}I 530 keV	1.42	1.43	± 3.8	± 2.4
	^{132}I 773 keV	9.21	9.20	± 3.9	± 3.3
	^{97}Nb 658 keV	2.46	2.47	± 1.6	± 2.1
	^{97}Nb 743 keV	2.44	2.46	± 4.8	± 2.5

Average standard deviation ± 2.7% ± 1
Average counting statistical error ± 2.13%

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[a] $R_j = {}^{239}\text{Np}/\text{f.p. gamma peak}$; $F = {}^{235}\text{U}/{}^{238}\text{U}$

[b] Slope of the R_j vs. 1/F line as calculated by least squares analysis.

statistics alone to that calculated from the R_jF product revealed that counting statistics are the major source of error. However, there is an indication of an additional error probably due to peak integration, but the number of analyses carried out is not sufficient for evaluation.

To simplify the treatment of the results, a table similar to Table 1 was constructed for each sample. The values shown in the top row and in the first column can be compared with the "standard" average relative intensities given in Table 2 and 3. Deviations larger than the assumed margin of error can then be used to identify instrument or calculation errors in the determination of the gamma-ray intensities. The remainder of the table gives the $^{238}U/^{235}U$ ratio as determined from the individual ^{239}Np/f.p. activity ratios read on the appropriate calibration curve.

IV. References

[1] Cali, J. P., Weiner, J. R., and Rocco, G. G., Modern Trends in Activation Analysis, College Station, Texas, 1965, p. 253.

[2] Kjelberg, A., Pappas, A. C., and Westgaard, L., Radioch. Acta **5**, 104 (1966).

[3] Amiel, S., Anal. Chem. **34**, 1683 (1962).

[4] Hollander, J. M., Nucl. Instrum. Methods **43**, 65 (1966).

[5] Guzzi, G., Pauly, J., Girardi, F., and Dorpema, B., Euratom Report EUR-3468^e (1967).

[6] Hyde, K. E., Perlman, I., Seaborg, G. T., in The Nuclear Properties of the Heavy Elements, Vol. II, Prentice Hall Inc., New Jersey, 1964, p. 437.

[7] Moore, L. F., Anal. Chem. **29**, 941 (1957).

PULSED NEUTRON ACTIVATION ANALYSIS SYSTEM FOR SHORT-LIVED RADIOISOTOPES

W. F. Naughton and W. A. Jester

The Pennsylvania State University
Nuclear Reactor Facility
University Park, Pennsylvania

I. Introduction

Extremely accurate short half life activation analysis has been relatively difficult to attain with radioisotopes having half lives as low as a few seconds due mainly to difficulties in sample handling and analysis. Many other problems besides that of rapid decay exist for the experimentalist concerned with sensitive and accurate determinations of short-lived radioisotopes. High and varying resolving times in counting the irradiated specimens, precision timing of the irradiation, decay and count times of each specimen, and spectral interferences due to the presence of other constituents in the sample container or due to the contamination of the specimen container are a few of the other problems confronting the experimentalist.

Despite these numerous difficulties there is now becoming available to the experimentalist engaged in short half life activation analysis a powerful research tool—reactor systems with pulsing capability. For it is of importance to note that a single reactor pulse will induce more short-lived activity than continuous irradiation to saturation at the normal reactor power level [1]. At the same time, the amount of long-lived activity resulting from the pulse is an extremely small portion of its steady state saturated activity. Therefore, using the pulse mode of operating, the experimentalist not only greatly enhances the short-lived activity but also suppresses the activation of the long-lived radioisotopes and thereby lowers the limit of detection of the analysis.

To further aid the experimentalist, most reactor facilities and research centers possess rapid pneumatic transfer systems capable of returning a sample from the reactor core to a fume hood or counting laboratory for analysis in one to five seconds [1-3]. Unfortunately, valuable time is usually lost in transferring the irradiated specimen from the transfer container (rabbit) to the counting position, significantly reducing the activity of interest. The other alternative is to count the sample in the rabbit but this has usually become contaminated and then activated in its transit, thus increasing the sample background. The existing Pennsylvania State TRIGA Reactor (PSTR) Pneumatic transfer system fell into the first category [4]. It is capable of returning an irradiated sample from the reactor core within three to four seconds. However, the actual time before analysis commences ranges from ten to twenty seconds, depending solely on the experience and dexterity of the experimenter in transferring the specimen from the rabbit to its counting position near the gamma scintillation detector. Consequently, to be able to accurately analyze isotopes with half lives of a few seconds or less, the experimentalist had either to devise an entirely new system or to modify existing systems.

Thus, a research program was undertaken for the design and modification of the existing PSTR system to make it capable of handling and analyzing short-lived radioisotopes with half lives as low as one to two seconds. As part of this program, the pneumatic transfer system is being instrumented so that the irradiation time, decay time, and count time of each sample can be measured to a tenth of a second accuracy, allowing accurate quantitative analyses involving short-lived radioisotopes.

II. Experimental

A. Apparatus

The major designs and modifications incorporated into the PSTR Pneumatic system and rabbits are illustrated in Figure 1 which is a schematic of the modified laboratory receiver. Upon impaction of the rabbit on the stainless steel knife edge, it allows the immediate passage of the irradiated sample and its container to the detector position via the in-shield terminus assembly. The separation mechanism consists of a slotted circular stainless steel knife edge upon which the rabbit impacts. The rabbit has a modified cap containing a thin replaceable polyethylene diaphragm which is screwed down over a polyethylene washer. Upon impaction, the strip severs, leaving the contaminated rabbit impaled on the knife. The circular knife is made from a section of stainless steel pipe so that the sample falls through its center and into the counting position.

B. Procedure

Upon completion of the modifications to the PSTR system, some preliminary experiments with both in-core termini (bare and cadmium lined) were designed to evaluate the system's performance before any quantitative measurements were attempted. The bare terminus is utilized

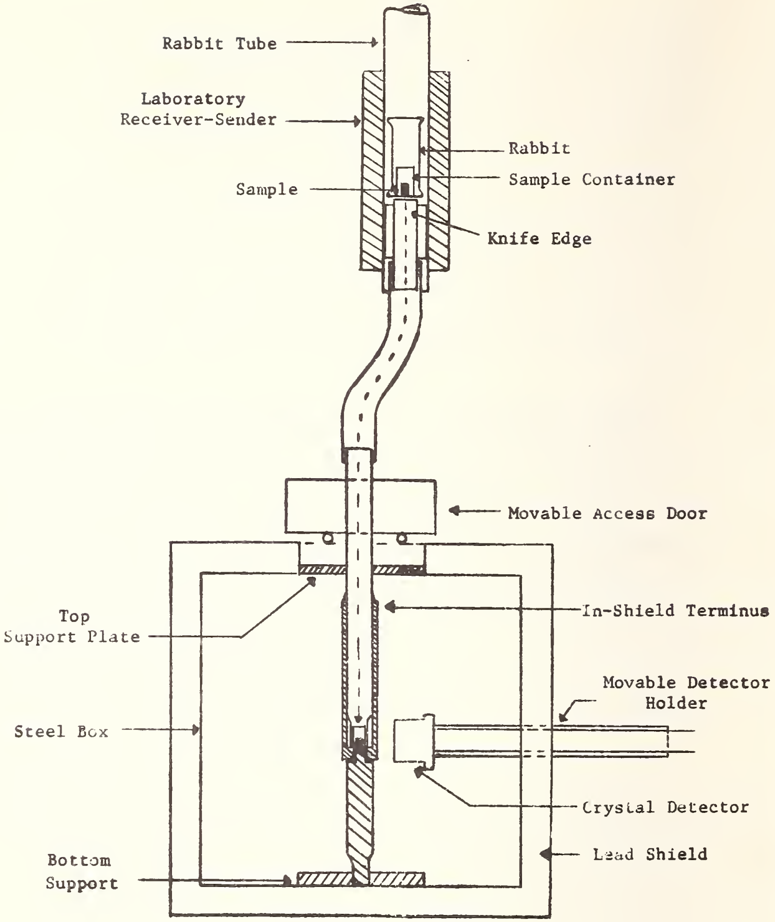

Figure 1. Schematic of modified receiver and in-shield assembly.

primarily for thermal activation (n,γ), whereas the cadmium lined terminus is employed when fast neutron reactions are sought. Fast neutron reactions are especially useful in the analysis of light molecular weight elements. The maximum pulse currently available at the PSTR is a 1000 MW (peak power) pulse, which gives an enhancement over steady state activation at 1 MW for all radioisotopes having half lives of thirty seconds or less. Preliminary testing led to the discovery of a major problem in thermal pulse activation. It was found that the small sample container (polyethylene vials) contained considerable trace quantities (about 100 μg) of aluminum, producing a strong background gamma spectrum of the 2.30 minute aluminum-28 radioisotope. Consequently, short-lived activation analysis with the bare terminus was limited to those radioisotopes with photopeak energies above that for aluminum-28 or those which produced stronger gamma spectra than the ^{28}Al of the vials. However, activation of these polyvials in the cadmium lined terminus, which suppresses the thermal flux by a factor of about 18, resulted in a comparable reduction in the aluminum-28 background. Consequently, the initial experimental procedures were formulated to analyze quantitatively a few of the important fast neutron reactions with short-lived products and to establish limits of detection for these reactions using this system.

Most of the reported sensitivities or limits of detection are from research centers utilizing charged particle accelerators and neutron generators. As a result, a few of the more prominent reactions were selected to ascertain whether comparable sensitivities could be obtained with the modified PSTR system. Each element selected for analysis was irradiated in the rabbit terminal centered on a core face in a pulse with a peak power of 1000 MW (megawatts). It is expected that greater sensitivities will be obtained when larger pulsing capability becomes available and when the rabbit terminal is moved in-core to higher flux positions.

III. Results and Discussion

A. RESULTS

The detection limits obtained through activation by the pulse method are illustrated in Table 1. It also compares the results obtained with the PSTR system to those made with a 150 kV accelerator [5].

Table 1. Limits of detection for a few short–lived neutron reactions.

Element	Reaction	Product	Half life	Gamma–ray energy (MeV)	PSTR[a] detection limit (μg)	150 KV[b][5] accelerator limit (μg)
^{16}O	(n, p)	^{16}N	7.35 sec	6.13	54.8[c]	75
^{19}F	(n, α)	^{16}N	7.35 sec	6.13	0.23[c]	150
^{19}F	(n, γ)	^{20}F	11.0 sec	1.63	0.19	–
^{23}Na	(n, p)	^{23}Ne	38.0 sec	0.44	1.8	100
^{23}Na	(n, α)	^{20}F	11.0 sec	1.63	8.0	100
^{34}S	(n, p)	^{34}P	12.4 sec	2.1	150	7000
^{31}P	(n, α)	^{28}Al	2.30 min	1.78	2.6	190

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[a] PSTR basis
Counts started 5 seconds after a 1000 MW pulse.
Detection limit defined as 100 counts/photopeak (± 10%).

[b] 150 KV accelerator basis
Three second wait time after activation.
Detection limit defined as ± 20%.

[c] Net counts obtained in 3.5 to 7.0 MeV range.

The elements chosen for activation were selected for specific reasons. Many researchers and manufacturers have expressed considerable interest in nitrogen, fluorine, and oxygen. For example, the important effects of oxygen content on physical properties of materials and the wide distribution of this element in nature necessitates a rapid and reasonably accurate method for trace oxygen determination free of matrix interferences [6]. Similarly, rapid analyses for sodium can be made routinely utilizing the fast neutron reactions in which there is a negligible amount of the longer-lived activity activated in the sample. Sulfur and phosphorus are two of the more troublesome elements which are not very easily detectable when both are present in similar amounts in the same specimen, since the major activation product of the two is the 14.3 day β (beta) emitter ^{32}P. However, with utilization of the pulse mode of operation and their respective fast reactions, both can be rapidly analyzed together.

B. DISCUSSION

Hence, it has been demonstrated that utilization of the pulse mode of operation of a research reactor in conjunction with an adequately instrumented fast pneumatic system results in excellent sensitivity for some of the fast neutron reactions of some of the lower molecular weight elements and has potentially a much greater sensitivity for many thermal neutron reactions producing short-half-lived radioisotopes once proper sample containers are available.

IV. References

[1] Guinn, V. P., "Reactor-Produced Short-Lived Radioisotopes Used in Neutron Activation Analysis", Production and Use of Short-Lived Radioisotopes From Reactors, Vol. 2, International Atomic Energy Agency, Vienna, 1963, pp. 20-22.

[2] Meinke, W. Wayne, "Pneumatic Tubes Speed Activation Analysis", Nucleonics **17,** 9, 87 (1959).

[3] Steele, Edgar L., and Meinke, W. Wayne, "Fast Neutron Activation Analysis", Proceedings 1961 International Conference on Modern Trends in Activation Analysis, College Station, Texas 1961, pp. 161-165.

[4] O'Brien, John, "The Pennsylvania State University PSR Pneumatic Transfer System", Nuclear Reactor Facility Report No. PSR315-496548, The Pennsylvania State University, August 1964.

[5] Perdijon, Jean, "Experimental Sensitivities in Neutron Activation and Gamma Spectrometry with a 150-kV Accelerator", Anal. Chem. **39,** 448-456 (1967).

[6] Steele, Edgar L., and Meinke, W. Wayne, "Determination of Oxygen by Activation Analysis with Fast Neutrons Using a Low-Cost Portable Neutron Generator", Anal. Chem. **34,** 185 (1962).

THE DETECTION AND DETERMINATION OF FISSIONABLE SPECIES BY NEUTRON ACTIVATION–DELAYED NEUTRON COUNTING [1]

James L. Brownlee, Jr.

University of California
Lawrence Radiation Laboratory
Livermore, California

I. Introduction

The detection and determination of fissionable species at trace levels has been a problem encountered in a number of areas of research. In the past, the activation analysis approach to the determination of fissionable nuclei has been directed primarily along two avenues of approach: (1) (n,γ) activations, followed by radioassay of the primary product (for example ^{238}U (n,γ) ^{239}U, ^{232}Th (n,γ) ^{233}Th), or possibly radioassay of the active daughter of the primary product, as with $^{239}\mathrm{U} \rightarrow {}^{239}\mathrm{Np} \rightarrow {}^{239}\mathrm{Pu}$, and $^{233}\mathrm{Th} \rightarrow {}^{233}\mathrm{Pa} \rightarrow {}^{233}\mathrm{U}$; and (2), use of the (n,f) reaction, with radioassay of one or more of the longer-lived fission products. Each of these approaches suffers from the necessity for radiochemical separations which can be time consuming, from interferences encountered in the application of nondestructive gamma spectrometry, even when high resolution Ge(Li) detectors are used, and/or interferences caused by the presence of more than one fissioning specie. Other nonradiochemical techniques have also suffered from their own unique disadvantages when applied to trace-level determinations, especially in a complex matrix (for example, the long exposures required in spark source mass spectrometry).

The utilization by Amiel [1], and by investigators at Oak Ridge [2] of the delayed neutron emitters found among the fission products for fissionable specie analysis has eliminated a number of problems. Since these delayed neutron emitters are short-lived, chemical separations are, at best, impractical. On the other hand, the fact that neutrons can be detected with reasonably good efficiency and free of gamma interference makes chemical separation unnecessary. In the investigations mentioned above, gross counting of delayed neutrons was used to determine a single fissionable specie whose presence has been detected by other means.

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[1] Work performed under the auspices of the U.S. Atomic Energy Commission.

Where sufficient differences exist in the cross sections for fission as a function of neutron energy, two species can be determined when both are present in a mixture. In this application, two irradiations are performed on each sample, one with, and one without, cadmium covers. Sensitivities are limited both by the relatively low epithermal and the fast neutron cross sections, and by the relatively low epithermal and fast fluxes available in many reactor facilities.

The "differential irradiation" technique is limited by practicalities to one, or at best, two fissionable species. It is often necessary, as for example in radiochemical diagnostics, to determine more than two species present in a complex matrix. The method reported upon below can be applied to the determination of two *or more* species with limits of detection in the tens-of-nanograms region for the thermal fissioning species (^{233}U, ^{235}U and ^{239}Pu) and with higher limits of detection for the fast fissioning species, and makes use of a single irradiation per sample. In addition, preliminary results indicate that qualitative knowledge of the fissionable species present is not always necessary, but may be obtained from the decay data.

II. Experimental

A. APPARATUS

Irradiations of standards and samples were carried out at the Livermore Pool-Type Reactor (LPTR). Initial irradiations were conducted using a short vacuum-type pneumatic tube system with a thermal flux of $1.2 \times 10^{13} n \cdot cm^{-2} \cdot sec^{-1}$ and a cadmium ratio of 2.0. Since the tube exit is approximately 300 feet away from the neutron counting system, a 45-second delay before counting was necessary for sample transfer. Subsequent irradiations were made using a newly installed pressure-operated pneumatic transfer system, allowing samples to be returned directly into the neutron counter with transit times of a few seconds.

The detection system employed in these studies has been described in part elsewhere [3]. Briefly, it consists of an array of forty $^{10}BF_3$ proportional detectors imbedded in a lattice of reactor grade graphite forming a right circular cylinder five feet in diameter and six feet long. This entire array is surrounded by two feet of water, which acts as both reflector and shield, and is operated with neutron-emitting sources positioned at the center. Materials such as beryllium and organic moderators were carefully excluded to prevent the possibility of exciting photoneutron emission with gamma radiation emitted by the sample. The detector tubes are arranged in six concentric rings outward from the center. Their outputs are fed to forty independently adjustable preamplifiers, then mixed by ring to be counted by six 10 MHz scalers.

The output of each ring is further mixed to provide a total count and to provide an input to a 4096-channel pulse-height analyzer/multiscaler which is used to record the delayed neutron decay curve. The scalers and the multichannel scaler are started simultaneously from a single switch.

B. PROCEDURE

Standards and samples are sealed in a primary container of polyethylene. This capsule is inserted in an irradiation capsule along with a flux monitor and irradiated, typically for one minute. On return to the neutron counter, the delayed neutrons are counted for ten minutes on the individual scalers. Simultaneously, the entire delayed neutron decay curve is recorded on the multiscaler, typically using 1024 channels of its memory, with dwell times of 1 second or less per channel. Once the delayed neutron emitters have decayed to background, the flux monitor is removed from the capsule for counting. In order to correct for short term drifts in the detection system, a calibrated spontaneous fission source is counted before and after each sample.

III. Discussion and Results

The decay with time of delay neutron activities can be represented by a linear summation of exponential decay groups. Thus the activity, Y, recorded in the Nth time channel of a multichannel scaler can be represented by:

$$Y(N) = \sum_{J} (A(J) \exp(-\lambda(J) T(N))) \tag{1}$$

where $\lambda(J)$ is the decay constant (sec^{-1}) of the Jth delayed neutron group, $A(J)$ is the zero-time activity of the Jth group, and $T(N)$ is the time, measured from the end of the irradiation, at the start of the Nth counting interval. As has been pointed out in the literature [4], despite the probable existence of as many as two dozen delayed neutron emitters among the fission products, the optimum least-squares fit to experimental decay data is obtained using only six half life groups, having the following (approximate) values:

Group index	Approximate half–life (sec)
1	55
2	22.5
3	5.4
4	2.3
5	0.5
6	0.2

As might be expected from a consideration of the fission process, the delayed neutron activities formed from all of the fissioning species possess essentially the same half lives for the various groups. The small differences that appear to exist in these group half lives from one fissioning species to another are sufficiently small as to preclude their use in the resolution of the decay curve from a mixed source. This is amply illustrated by the data of Table 1. As a consequence, the disintegration constants, $\lambda(J)$, of equation (1) can be replaced by weighted average values when the $Y(N)$ represent decay activities from a mixed source. The zero-time activities of the various delayed neutron groups, $A(J)$, then become summations of the zero-time activities of the various components, and can be represented by:

$$A(J) = \sum_I \frac{w(I)}{W(I)} N_0 \phi \sigma(I) \epsilon (AB(I,J)) S(J) C(J) \qquad (2)$$

where

$w(I)$ = weight in grams of the Ith isotope
$W(I)$ = atomic weight of Ith isotope
N = Avogadro's number
ϕ = neutron flux, $n \cdot cm^{-2} \cdot sec^{-1}$
$\sigma(I)$ = fission cross section of Ith species
ϵ = counting efficiency
$AB(I,J)$ = absolute yield of delayed neutrons of the J half life group per fission of the Ith (fissioning) species.

$S(J)$ is the saturation term for the Jth half life group for an irradiation period of T_b seconds, and is given by

$$S(J) = 1\text{-}\exp(-\lambda(J) T_b) \qquad (3)$$

$C(J)$ accounts for the fact that the activities are not instantaneous values, but are recorded for a finite time interval, T_c:

$$C(J) = 1\text{-}\exp(-\lambda(J) T_c)/\lambda(J) \qquad (4)$$

In practice, then, the analysis depends upon differences in the delayed neutron group abundances from one specie to another, rather than differences in half life, as is the usual case.

The actual least squares resolution and analysis of the decay curve data are performed by computer matrix reduction of weighted counting data. The program yields $A(J)$ values for each delayed neutron group present in the decay curve, with least squares propagated errors typically ranging from a few tenths to ten percent, depending upon total activity. These $A(J)$ values are then used to generate a series of equations (2), which are then solved for individual $w(I)$ values. Results on known mixtures of two

Table 1. Delayed–neutron half lives and yields.[a]

A. Thermal Fission

Group index J	^{235}U(99.9% 235)		^{239}Pu(99.8% 239)	
	Half life seconds	Absolute group yield, %	Half life seconds	Absolute group yield, %
1	55.72 ± 1.28	0.052 ± 0.005	54.28 ± 2.34	0.021 ± 0.006
2	22.72 ± 0.71	0.346 ± 0.018	23.04 ± 1.67	0.182 ± 0.023
3	6.22 ± 0.23	0.310 ± 0.036	5.60 ± 0.40	0.129 ± 0.030
4	2.30 ± 0.09	0.624 ± 0.026	2.13 ± 0.24	0.199 ± 0.022
5	0.610 ± 0.083	0.182 ± 0.015	0.618 ± 0.213	0.052 ± 0.018
6	0.230 ± 0.025	0.066 ± 0.008	0.257 ± 0.045	0.027 ± 0.010
	^{233}U(100% 233)			
1	55.00 ± 0.54	0.057 ± 0.003		
2	20.57 ± 0.38	0.197 ± 0.009		
3	5.00 ± 0.21	0.166 ± 0.027		
4	2.13 ± 0.20	0.184 ± 0.016		
5	0.615 ± 0.242	0.034 ± 0.016		
6	0.277 ± 0.047	0.022 ± 0.009		

B. Fast Fission

	^{235}U(99.9% 235)		^{239}Pu(99.8% 239)	
1	54.51 ± 0.94	0.063 ± 0.005	53.75 ± 0.95	0.024 ± 0.002
2	21.84 ± 0.54	0.351 ± 0.011	22.29 ± 0.36	0.176 ± 0.009
3	6.00 ± 0.17	0.310 ± 0.028	5.19 ± 0.12	0.136 ± 0.013
4	2.23 ± 0.06	0.672 ± 0.023	2.09 ± 0.08	0.207 ± 0.012
5	0.496 ± 0.029	0.211 ± 0.015	0.549 ± 0.015	0.065 ± 0.007
6	0.179 ± 0.017	0.043 ± 0.005	0.216 ± 0.017	0.022 ± 0.003
	^{238}U(99.98% 238)		^{240}Pu(81.5% 240)	
1	52.38 ± 1.29	0.054 ± 0.005	53.56 ± 1.21	0.028 ± 0.003
2	21.58 ± 0.39	0.564 ± 0.025	22.14 ± 0.38	0.238 ± 0.016
3	5.00 ± 0.19	0.667 ± 0.087	5.14 ± 0.42	0.162 ± 0.044
4	1.93 ± 0.07	1.599 ± 0.081	2.08 ± 0.19	0.315 ± 0.027
5	0.490 ± 0.023	0.927 ± 0.060	0.511 ± 0.077	0.119 ± 0.018
6	0.172 ± 0.009	0.309 ± 0.024	0.172 ± 0.033	0.024 ± 0.005
	^{233}U(100% 233)		^{232}Th(100% 232)	
1	55.11 ± 1.86	0.060 ± 0.003	56.03 ± 0.95	0.169 ± 0.012
2	20.74 ± 0.86	0.192 ± 0.009	20.75 ± 0.66	0.744 ± 0.037
3	5.30 ± 0.19	0.159 ± 0.025	5.74 ± 0.24	0.769 ± 0.108
4	2.29 ± 0.18	0.222 ± 0.012	2.16 ± 0.08	2.212 ± 0.110
5	0.546 ± 0.108	0.051 ± 0.010	0.571 ± 0.042	0.853 ± 0.073
6	0.221 ± 0.042	0.016 ± 0.005	0.211 ± 0.019	0.213 ± 0.031

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[a] Data abstracted from Ref. 4 p. 86, 87 ,90.

fissionable species indicate that results can be obtained to an accuracy of the order of ±20% at the part per million (ppm) and lower levels.

Identification of the component fissionable species in a mixture seems feasible, based in part upon ratios of *A(J)* values for the various pure species. In examining data obtained from a series of standards of ^{239}Pu and ^{235}U in thermal fission, it has been noted that the ratio A(2):A(1) has a value 9.25 for ^{235}U and 13.88 for ^{239}Pu. These data were obtained over a range of sample weights from 0.1 to 10 μg by the least squares technique. The value of the ratio for ^{233}U should be approximately 4.79. Thus it should be possible, by examining experimental *A(J)* ratios, to obtain tentative identification of the component fissionable species. In cases where decay data alone leaves the composition unresolved, it has been found [3] that the ratio of the sum of counts in rings 1 and 2 to the sum of counts in rings 5 and 6 of the neutron detector system can be used to estimate neutron energies. With these pieces of data, plus the fact that the average delayed neutron energy is a function of average fission chain length, and hence of the fissioning species [4], more certain identification can be made.

IV. References

[1] Amiel, S., Anal. Chem. **34**, 1683-92 (1962).

[2] Dyer, F. F., Emery, J. F., Leddicotte, G. W., U.S. Atomic Energy Commission, Report ORNL-3342, 16 Oct. 1962.

[3] Jewell, R. W., John, W., White, D. H., Nuclear Inst. Methods, in press.

[4] Keepin, G. R., Physics of Nuclear Kinetics, Ch. 4, Addison-Wesley, Reading, Mass., 1965.

A HIGH-INTENSITY ^{241}Am-Be-^{242}Cm NEUTRON SOURCE [1]

M. Wahlgren, J. Wing, and D. C. Stewart

Chemistry Division
Argonne National Laboratory
Argonne, Illinois 60439

I. Introduction

A set of eight high intensity isotopic neutron source slugs has been prepared by irradiation of ^{241}Am-Be capsules in the Material Testing Reactor to produce ^{242}Cm. At the end of irradiation each capsule emitted approximately 1.2×10^9 neutrons per second. This type of isotopic neutron sources produces a spectrum of unmoderated neutrons primarily in the 4-8 MeV energy range. The new sources and source holder have been designed to give improved geometry for fast neutron irradiations, compared to the original assembly reported by Mohr, Wahlgren, and Stewart [1].

The capsule and source holder design are described and the features of the irradiation assembly are discussed. The factors considered in selection of irradiation flux and time for production of the source capsule are reviewed. An estimate is presented for the current cost of production of this type of source. The analysis for fluorine by the $^{19}F(n,\alpha)^{16}N$ reaction has been studied using the isotopic source and found to be almost interference-free. Optimized sensitivities for 60 chemical elements using the unmoderated source neutrons have been determined.

II. Experimental

A. ^{241}AM-BE CAPSULE DESIGN

In order to get the maximum unmoderated neutron flux the source holder was designed to give closest packing of six sources surrounding the central rabbit tube. The coaxial design provides a minimum flux gradient across the sample, and the multiple source arrangement also facilitates source handling and cooling.

The source capsules are 1.58 cm in diameter by 3.82 cm long, and contain a 1 cm^3 void volume to prevent possible pressure buildup due to fission gases from ^{242}Am and helium from the decay of ^{242}Cm.

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[1] Work performed under the auspices of the U.S. Atomic Energy Commission.

The ^{241}Am-Be capsules were prepared for Argonne by the Livermore Radiation Laboratory. Each capsule contained approximately 1 gram of ^{241}Am as oxide mixed with 200 mesh beryllium metal in the atom ratio Be:Am of 50:1. The neutron emission rate after fabrication, but prior to irradiation, averaged 5.6×10^6 neutrons per second per gram of americium. This value is fairly close to the figure of 6.2×10^6 neutrons per second per gram reported by Jordan and Schierling [2].

B. ^{241}AM-BE CAPSULE IRRADIATION

By reference to the heavy element buildup curves of Stewart, *et al* [3] it is seen that the maximum yield of ^{242}Cm would be obtained at a flux of $7 \times 10^{14} \text{n}\cdot\text{cm}^{-2}\cdot\text{sec}^{-1}$, which is attainable in several present-day reactors. Heat transfer calculations [4] for the 1.58 cm diameter by 3.82 cm long capsules at the heat generation rate [3] predicted for the initial stages of irradiation at this flux indicated capsule core temperatures of several thousand degrees might be expected. This consideration was the limiting factor in selecting the neutron flux to be used for the irradiation of the capsules.

It was decided to irradiate the sources for 7 fuel cycles (126 days of irradiation) in the Materials Testing Reactor at a flux of $8 \times 10^{13} \text{n}\cdot\text{cm}^{-2}\cdot\text{sec}^{-1}$. The heavy element production computations indicate a conversion of about 25% of the ^{241}Am to ^{242}Cm would be expected for this irradiation. For a typical slug this would result in production of 0.25 gram of ^{242}Cm. The neutron emission rate would be increased to 1.4×10^9 neutrons per second due to the high specific activity of the ^{242}Cm product. In addition, Runnals and Boucher [5] have found the neutron output to be a function of the alpha particle energy E as given by the expression, $n_{max} = 0.152\, E^{3.65}$ neutrons per million alphas. For the case of the isotopes ^{241}Am and ^{242}Cm, this dependence would bring the neutron emission rate to $2.2 \times 10^9 \text{n}\cdot\text{sec}^{-1}$, which is almost twice the experimentally determined value of $1.2 \times 10^9 \text{n}\cdot\text{sec}^{-1}$. The discrepancy is due primarily to neutron self-shielding of the sample, since the ^{241}Am target has cross sections of 50 and of 600 barns for the production of the isomers of ^{242}Am.

C. SOURCE HOLDER ASSEMBLY

Six capsules have been installed in a stainless steel source holder-rabbit tube assembly (See Figure 1) which is housed in an 18 in. diameter by 48 in. high water tank shield. The water tank is lowered into a storage pit in the floor of a shielded cell. The shielding provided by the 42 in. of water is sufficient to reduce the gamma and neutron leakage to low levels. A close-up view showing the details of the source holder is given by Figure

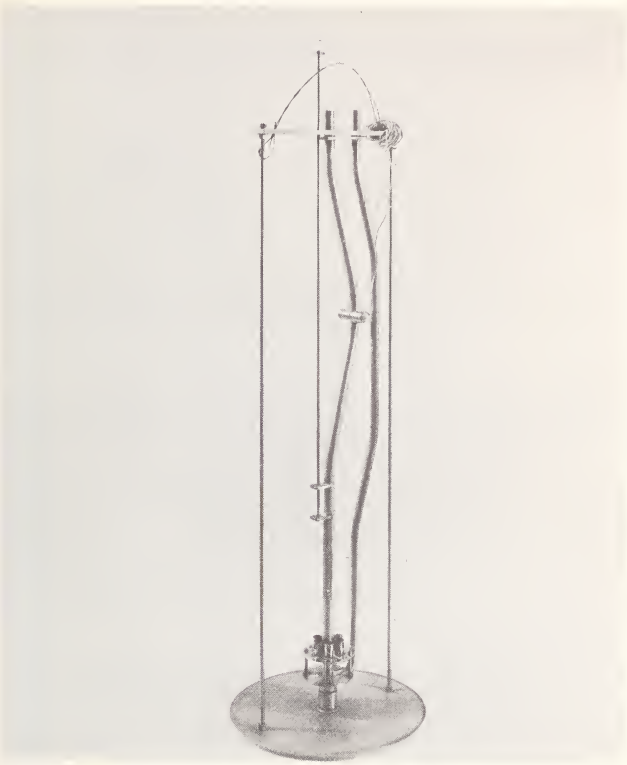


Figure 1. Isotopic neutron source holder and rabbit assembly.

2. Accurate positioning of the sources in the holders is provided by the spring tab formed by the cut-out in the stainless steel source holder.

The water in the shielding tank is continuously recirculated through a filter unit. A liquid level sensor is set to indicate low coolant and shielding *via* an audible alarm when the level drops to 6 in. below the normal filling level.

The rabbit capsule used in this assembly is 19 mm diameter and has a volume of 8 cm^3. The central rabbit tube is surrounded by a 30 mil cadmium sleeve which can be lowered or raised as required. This permits absorption of thermal neutrons by the Cd for samples where thermal neutron activation produces interference.

A light beam and photocell are used to monitor the exact time of start of irradiation of samples. The programmer previously described [1] was modified to advance from "transit to target" function to the "irradiate" function as soon as the photocell output is received. This eliminates a potential timing uncertainty which could lead to poor precision and accuracy.

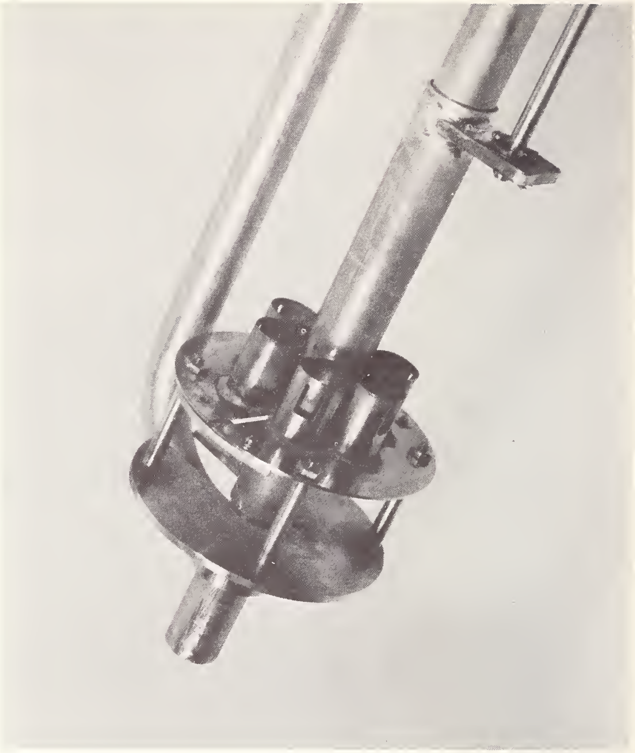


Figure 2. Close-up view showing detail of source holder.

D. COST ESTIMATION

The cost breakdown for the present set of sources is as follows: 6 grams ^{241}Am, $9000; capsule fabrication, $3600; irradiation charge, $2200; and handling and shipping charges, $600.

III. Results and Discussion

A. RESULTS

The relative detection sensitivities for 73 chemical elements utilizing the unmoderated neutrons from a prototype source assembly were previously reported by Wing and Wahlgren [6]. A summary of experimental sensitivities optimized for about 60 of these elements has been prepared using the new source assembly and submitted for publication [7].

Of a number of activation experiments under way, the analysis of fluorine by the $^{19}F(n,\alpha)^{16}N$ reaction appears to be very useful. The observed sensitivity is 4.8×10^4 counts per gram of fluorine ($t_{irr} = 30$ sec, $t_{decay} = 4$ sec, $t_{count} = 30$ sec, fast neutron output 5×10^9 n/sec, fast neutron flux of $1.4 \times 10^8 n \cdot cm^{-2} \cdot sec^{-1}$). No interference is observed from oxygen present in the sample since the threshold of the $^{16}O(n,\alpha)^{16}N$ is higher than the available neutron energies. This work has also been submitted for publication [8].

Other projects currently under study are symmetric/asymmetric fission yields, and rapid analysis of rock samples by activation. Neutron capture gamma-ray studies along the lines of that reported by Mandler and Terrell [9] using the prototype ANL sources are also planned. One of the sources is being evaluated for neutron radiography by Berger and Barton [10].

B. Discussion

It does not appear practical to make a source greater than 5×10^{10} neutrons per second by the present technique. Taking sample neutron self-shielding into account, it should be possible to irradiate at a flux of at least $1.5 \times 10^{14} n \cdot cm^{-2} \cdot sec^{-1}$ without excessive heat buildup. The use of an americium-beryllium alloy [5] would double the specific neutron output, and also improve the heat transfer characteristic of the sample.

A price cut for ^{241}Am from $1500 to $1000 per gram effective January 1969 has been announced recently [11]. Production costs possibly as low as $15 per gram have been estimated by Lang, Deonigi, and Rohrmann [12] for the americium and curium by-products of power reactor fuel reprocessing. It thus appears that this type of isotopic neutron source may remain competitive with ^{252}Cf [13] for certain applications.

IV. Acknowledgments

The authors wish to acknowledge the assistance of W. C. Mohr with capsule design, M. Coops (Livermore) in providing the encapsulation facilities, and H. Harvey in the design of the source holder assembly and shield system.

V. References

[1] Mohr, W. C., Wahlgren, M. A., and Stewart, D. C., "Design of the Argonne Isotopic Source Neutron Facility," Proc. 13th Conf. on Remote Systems Technology, 1965, pp. 138-141.

[2] Jordan, E. D., and Schierling, H. E., Trans. Am. Nucl. Soc. 5, 286 (1962).

[3] Stewart, D. C., Anderson, R. W., and Milsted, J., "The Production of Curium by Neutron Irradiation of ^{241}Am," Report ANL-6935, November 1964.

[4] Mohr, W. C., private communication (1967).
[5] Runnals, O. J. C., and Boucher, R. R., Can. **34,** 949 (1956).
[6] Wing, J., and Wahlgren, M., Anal. Chem. **39,** 85 (1967).
[7] Wing, J., and Wahlgren, M., submitted to Appl. Spectry. (1968).
[8] Wing, J., and Wahlgren, M., submitted to Anal. Chem. (1968).
[9] Mandler, J. W., and Terrell, C. W., Trans. Am. Nucl. Soc. **10,** 30 (1967).
[10] Berger, H., and Barton, J., private communication (1967).
[11] Nuclear News, p. 25, June 1968.
[12] Lang, L. W., Deonigi, D. E., and Rohrmann, C. A., Nuclear Applications **3,** 665 (1967).
[13] Reinig, W. C., Nuclear Applications **5,** 24 (1968).

NEW FACILITIES FOR ACTIVATION ANALYSIS AT THE GRENOBLE CENTER FOR NUCLEAR STUDIES

J. Laverlochere

Centre d'Etudes Nucleaires de Grenoble
Grenoble, France

I. Introduction

Activation analysis research and applications were organized at the Nuclear Center of Grenoble in 1959 and have been developed in connection with industry and research organizations in France for a large variety of applications in the field of physical and biological science and technique. The purpose of this action is to develop and to improve the method and its applications as well as to give increased facilities to every user who wants to work with this method belonging or not to the French Atomic Energy Commission. In this way, techniques, systems for irradiation, chemistry, counting, and computing have been and are presently being developed; and a new Laboratory, which is under construction, will be used in the beginning of 1969.

II. Irradiation

A. Reactors

Irradiations are done in two light water swimming pool reactors: SILOE (30 MW) and MELUSINE (4 MW), with maximum neutron fluxes of 2×10^{14} and $3 \times 10^{13} n \cdot cm^{-2} \cdot sec^{-1}$, respectively. In 1967, a heavy water tank has been placed in the latter to improve the ratio of thermal/rapid flux and to lower the heating for activation analysis (AA). This tank allows routine irradiations with a pneumatic tube, (55 mm diameter, high density polyethylene rabbits) and also with aluminum cans for one or two week irradiations. This tank is about 50 cm × 50 cm × 60 cm and is placed at eight centimeters from the core. Fluxes are given in Table 1. In SILOE, a short pneumatic tube (4 seconds) has been placed in a thermal flux of $4.8 \times 10^{13} n \cdot cm^{-2} \cdot sec^{-1}$, and is used for irradiation times up to 25 minutes by using high density polyethylene rabbits and maintaining air circulation during irradiation.

Rotation of the rabbits has been studied to diminish the effect of the horizontal flux gradient, and a system using a special cover and

Table 1. Flux in the heavy water tank (Melusine reactor).

Distance from the core	Thermal flux $n \cdot cm^{-2} \cdot sec^{-1}$	Fast flux above 1 MeV	Ratio thermal/fast
30 cm (pneumatic)	6×10^{12}	10^{11}	60
37 cm (pneumatic)	3×10^{12}	4.5×10^{10}	66
52 cm (hole for cans)	10^{12}	4.6×10^{9}	200
67 cm (holes for cans)	1.5 to 2×10^{11}	4.8 to 6.6×10^{8}	300

compressed air will be installed at the end of 1968 to give a rotation speed between 100 and 200 r.p.m. This system will improve the precision of analysis and simplify the standardization. Irradiation facilities will be placed in the new heavy water reactor whose high thermal flux will be very interesting for high sensitivity analysis. These facilities include long and short irradiations and are recapitulated in Table 2.

Table 2. Characteristics of the irradiation positions planned in the new high reactor (heavy water).

Irradiation position	Thermal flux[a]	Fast flux	Heating (W/g)
Pneumatic tube (90 cm from the core)	2×10^{14}	10^{10}	0.1
Pneumatic tube (130 cm from the core)	5×10^{13}	5×10^{8}	0.1
Manual (one cycle irradiations = 40 days)	max 5×10^{14}	max 8×10^{10}	0.2

[a] flux = $n \cdot cm^{-2} \cdot sec^{-1}$.

B. Neutron Generator

The accelerator (400 kV – 2mA, SAMES type T) is used for 14 MeV and 3 MeV neutron activation analysis. The first purpose has been to improve the sensitivity, and we obtain now, for example, 3×10^4 counts per milligram of oxygen. The precision is under study (flux homogeneity, stability, dosimetry, irradiation and counting geometry, *etc.*) and improvements to obtain a better precision will be done when this assembly is installed in the new building.

C. CYCLOTRON

The Institute of Nuclear Science is finishing installation of a variable energy cyclotron close to the Nuclear Center, and an agreement as been reached to assign a part of the time of this machine to activation analysis research. This cyclotron will be running for users at the end of this year and will give alphas or protons from 15 to 60 MeV and deuterons from 7 to 30 MeV with an intensity of several tens of microamperes. An irradiation station for activation analysis is being installed on one of the beam lines. This station has been studied to allow an irradiation under vacuum with a rotation of the sample and is imbued with the principle of the pneumatic system of the Institute of Nuclear Physics in Lyon.

III. Chemical Separations

Several new facilities have been developed.

A. HOT CELL

This hot cell has been installed and equipped to perform analysis of high activation cross section matrices such as sea water, tantalum, tungsten, *etc.*, and has 20 cm thick lead walls. It is equipped with fifty containers for reagents and can be operated for separations by ion exchange, electrolysis, and extraction.

B. AUTOMATION

Apparatus for automatic ion exchange resin separations has been studied and is used for ten continuous different elutions. A complete apparatus is now under construction to treat simultaneously several columns *i.e.* several samples and standards.

C. RESIN SORTING

We have studied the influence of the grain size of the resins on the shape of the elution curves in order to reduce the time requirement for the separations or to increase the decontamination factor. Results have generated a large interest in resin sorting, and an automatic countercurrent apparatus has been designed for routine sorting of commercial resins. This technique is especially interesting for very pure material analysis, and for routine work, it allows a reduction in the time of a separation by a factor of ten.

IV. Counting

The standard equipment includes four 400-channel pulse-height analyzers associated with 76 mm × 76 mm NaI(Tl) detectors. One of these assemblies is connected with a 150 mm × 200 mm dia NaI(Tl) detector. A Ge(Li) detector, 5 cm^2 × 1 cm thick associated with a 4000 channel analyzer is used exclusively for qualitative analysis which seems presently to be the field in which this detector gives the most interest in a great variety of applications in activation analysis and in chemical separations.

V. Computation

The IBM 360-40 computer located in the Center has been used for the treatment of gamma-ray spectra for several years. Programs have been written and form a tool not only for activation analysis but also for general gamma-ray spectroscopic analysis both with and without analysis of half life. A special program has been devised for oxygen determination when measurements are done by the decay mode. In the near future the counting equipment and a teletype will be connected with the computer *via* a network under construction in the Center. This connection will be done through a smaller computer which is used especially for data acquisition and network interrogation.

VI. The New Laboratory

Chiefly undertaken to give better conditions for radiochemistry, to concentrate and improve the irradiation facilities, and to offer larger possibilities to external users, the new building will have schematically for activation analysis six active laboratories (75 m^2 each) with twenty-four hoods, one cold laboratory (100 m^2) and counting rooms (200 m^2). In a first step, five pneumatic tubes will be installed: two tubes (55 mm dia) and one tube (40 mm dia) in the Melusine reactor, one tube (100 mm dia) for irradiations with the cyclotron, and one tube for irradiations with the 400 kV accelerator. In a second step several tubes are provided for connection to the high flux reactor and to other irradiation machines planned on the Center area. The tube terminals in the new building except for the 400 kV accelerator, will be located in a special room from which the irradiated samples will be sent by a internal pneumatic network to each of the active laboratories. This transfer will be partly automatic. Active laboratories will be connected to counting rooms by pneumatic tubes.

A part of these laboratories will be reserved for scientists from outside the Center who want to use these AA facilities for their own research or routine analyses or who, for example, want to use short half-lived radioisotopes or cyclotron irradiations. The expansion of AA in France for last ten years has shown the necessity of such a facility to develop AA applications and routine analyses. This part of the laboratory will provide general service and will be open to industry and to research organizations.

THE NUCLEAR ANALYSIS PROGRAM OF THE NRL CYCLOTRON FACILITY

John A. Eisele and Reginald E. Larson

Naval Research Laboratory
Washington, D.C. 20390

The Navy owns and operates a 76-inch sector-focused cyclotron based on a modified ORIC design. Although the capability of this accelerator is conveniently summarized by stating its maximum performance of accelerating a beam of protons to 75 MeV, it is also capable of accelerating a large variety of ions over a wide range of energies.

In addition to the pure research in nuclear structure and nuclear reaction physics, service irradiations and isotope production, the staff has been encouraged to create a materials analysis capability to serve the other interests of the Navy such as oceanography, space science, chemistry, metallurgy and solid state physics, as well as the growing needs of other Government agencies.

The program is oriented primarily at cooperative research in which the staff can participate in the formulation of problems requiring the use of activation analysis techniques. Stepping across discipline boundaries leads frequently to important research results, and recent emphasis on increased study of the ocean and the interactions between the ocean and the atmosphere offers new opportunities for collaboration between physics, chemistry, biology, astronomy, meteorology and mathematics. These frequently are bonuses. New gamma rays, better energy values, and new activities lead to research papers as by products.

The cyclotron is capable of accelerating beams of protons, alpha particles and helium-3 nuclei. For this last isotope, a helium recovery system has been installed. These particles are all useful in either charged particle activation analysis or isotope production. The versatility of the cyclotron will enable one to pick the particle and select the energy for an optimum measurement in any specific case. At a later time, heavier ions will be accelerated for ion implantation work, and channeling studies will also be carried out. This sector-focused cyclotron is a variable energy machine, and the energy resolution of 0.5 percent is far better than with the classic cyclotron, and therefore, is well suited to precise reaction cross section measurements.

At the present time, we are still in the calibration stage and learning our capabilities. We are in the process of gathering reaction cross section data of elements useful in activation analysis such as Ca, Mg, Si and Sr.

Figure 1 shows a floor plan of the experimental wing of the cyclotron building. The cyclotron is in the central room and a beam of charged particles may be delivered to any one of three experimental rooms. Nuclear physics research is conducted in Rooms 2 and 3 with a beam that has been energy-analyzed by the 9-ft. radius analyzing magnet. The materials analysis program and irradiation facilities are located in Room 1 where the most intense beam of particles is available. Experiment Room 1 is shown in Figure 2.

A pneumatic tube is available in the wall of Room 1 and will deliver samples rapidly to a future beta-gamma counting room. A single-sample holder or in-line holder is contemplated for use with this pneumatic tube.

The on-line computer at the cyclotron building is an EMR 6050. There are also twin dual analogue to digital converters (ADC) interfaced with this computer to allow multidimensional analysis of data. This computer is a complete system capable of running any Fortran program when not in use on-line.

At the present time, the analysis equipment consists of a 4096 channel Nuclear Data Analyzer and a 10 cm³ Ge(Li) detector. There is capability also for beta spectroscopy and gamma-gamma coincidence studies.

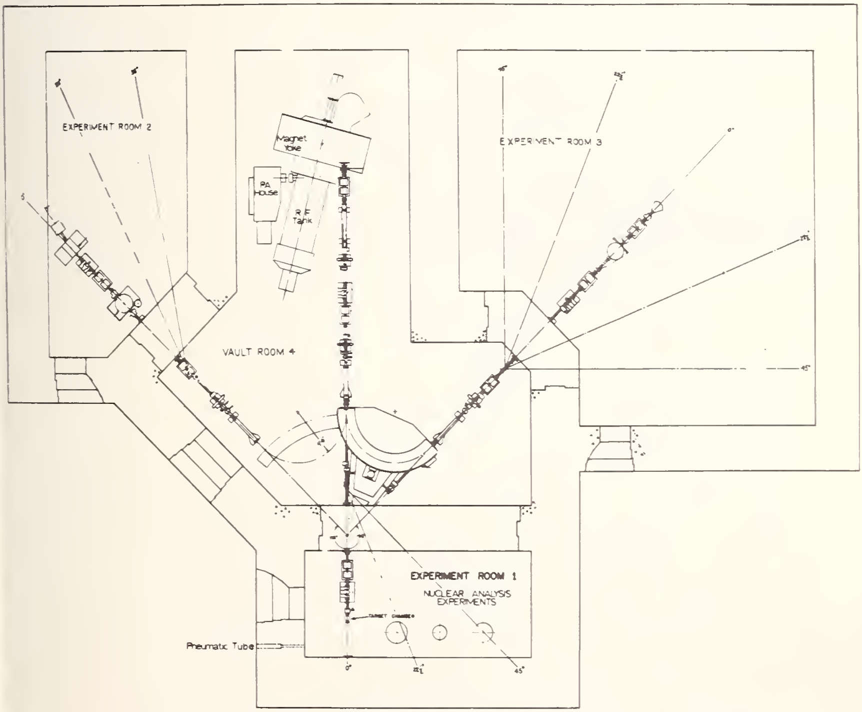


Figure 1. Floor plan of the experimental wing showing the location of the nuclear analysis facility.

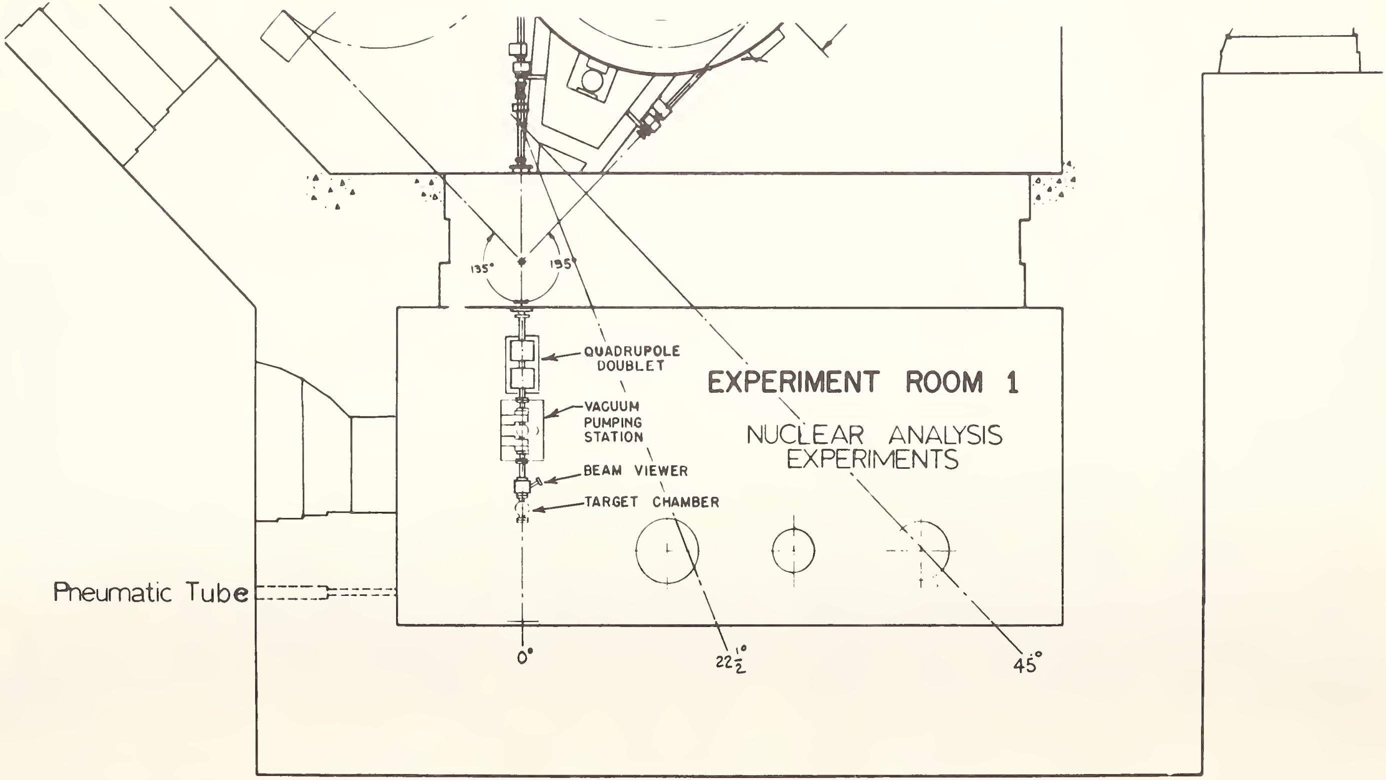


Figure 2. Expanded diagram of section Experimental Room No. 1 (see Fig. 1).

The first cooperative program is with the Nuclear Techniques Branch of the Ocean Sciences Division. Several samples of freeze-dried sea water salts and shells from marine animals have been irradiated by 12.5 MeV protons. With 12.5 MeV protons (p,n) is the primary reaction; thus, Na, Cl, Mn, and S are not appreciably activated. This opens the door for possible analysis of specimens for Ca and other elements present in small quantities without interference from Na, Cl, Mn, and S. There is no need for radiochemical separations. The short range of protons introduces a problem of changing cross section with depth in the sample, but may open some new possibilities.

At the present time, while waiting for completion of the beam transport system into Room 1, we have conducted some preliminary experiments with targets in the cyclotron vault. The target holder consists of a large rotating, water-cooled wheel with positions for sixteen samples. Our first experiment is to investigate the feasibility of using (p,n) reactions to study the (^{48}Ca/^{44}Ca) ratio. The variable energy will enable us to select the best proton energy to maximize the yield of the reaction products from the less abundant ^{48}Ca.

Two shell samples, bombarded with 12.5 MeV protons indicated isotope fractionation [(^{44m}Ca/^{48}Ca sample 1)] : [(^{44m}Ca/^{48}Ca) sample 2] of .950 ± .005; however, this was in the opposite direction than indicated by (^{44}Ca/^{48}Ca) ratios. This points out the importance of sample size and shape, and the necessity of developing techniques to maintain uniform thickness and density.

A sandwich consisting of seven layers of 10-mil calcium metal separated by 1-mil aluminum foil was irradiated with 12.5 MeV protons. The yields of ^{44m}Sc and ^{48}Sc are shown in Figure 3. The relative yield of ^{44m}Sc to ^{48}Sc, also shown in Figure 3, indicates the importance of maintaining uniform density and thickness of samples.

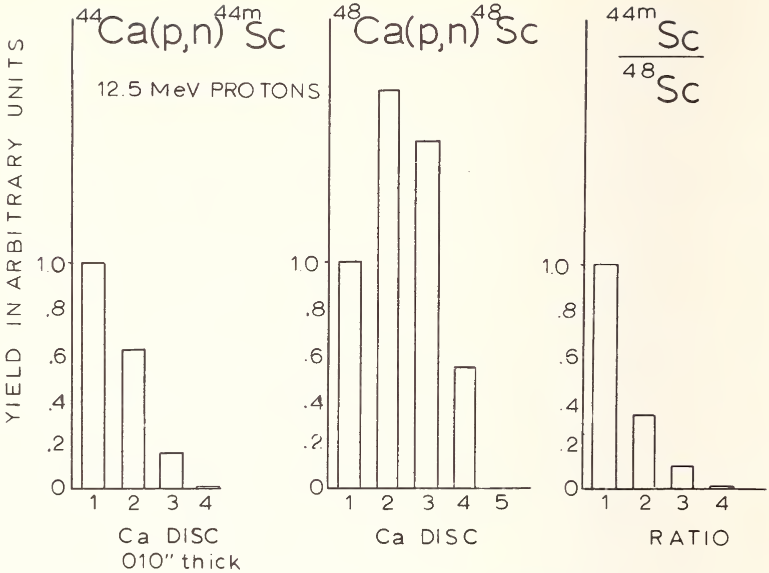


Figure 3. Relative yields of ^{44m}Sc/^{48}Sc.

THE LOCALIZATION OF IMPURITIES IN ACTIVATION ANALYSIS DEMONSTRATED BY ANALYSES OF SEMICONDUCTOR SILICON

J. Martin

Siemens Research Laboratories
Erlangen, Germany

I. Introduction

The interpretation of results obtained from highly sensitive activation analyses is made difficult by inhomogeneous distribution of the material to be analyzed. Errors due to this are particularly noticeable where comparisons are made with the results obtained by a second independent method of measurement having the same sensitivity. A typical case is the activation analysis of semiconductors. If the results are to be interpreted correctly, it is almost always necessary to locate the impurities by mechanical separation or by autoradiographs. Typical examples taken from practical experience in the analysis of high-purity silicon and silicon components are described and discussed below.

II. Experimental

The experimental investigation of neutron activated silicon is favored by its small activation cross section (σ_{act}=3 mb) and its short half life ($T_{1/2}$ 2.6 h). For activation neutron flux densities of approximately $5 \times 10^{13} n \cdot cm^{-2} \cdot sec^{-1}$ were employed. The necessary chemical separation was carried out by the methods due to Thompson, Strause and Leboeuf [1], and Gebauhr [2]. The radiochemical purity of the counting samples was measured, identified and checked in a gamma multichannel analyzer with a NaI detector.

The autoradiographs were taken with the films shown in Table 1, these being selected according to the activity present and the required resolution. A pressure of 200 g/cm^2 of the samples on the photographic emulsions sufficed for the x-ray films and the single-layer pack film. The stripping films were shrunk onto the samples in a moist expanded state by the normal method. Further details on the application of autoradiographs in semiconductor research are contained in a paper by J. F. Osborne [4].

Table 1. Sensitivity and resolution of films for radiographs.

Type of film	Make	Sensitivity ^{90}Sr disintegrations per cm^2 for S = 1	Resolution with ^{131}I test [3] (μm)
Double layer x–ray emulsion	Structurix D 10 Agfa Gevaert	1.7×10^6	40 – 50
Single layer pack film	Scientia 23D56, Agfa Gevaert	2.0×10^7	25 – 40
Stripping film	AR 50, Kodak	1.3×10^8	10 – 20
Stripping film	AR 10, Kodak	8.2×10^8	3 – 10

III. Results and Discussion

High purity silicon is normally obtained in polycrystalline form by the thermal decomposition and reduction of silanes of thin, heated rods of silicon. Activation analyses of fragments of such rods always produced greatly varying results even after careful etching of the irradiated samples. It was necessary to separate the edge and center of the rod mechanically to obtain reproducible results. Table 2 shows the results of the analysis of a bar of 20 mm diameter. As can be seen, copper, phosphorous and sulphur are present in greater concentration in the center. Approximately 5% arsenic is found in the center samples which corresponds to the percentage remaining on grown silicon after mechanical separation. If samples of the same rod are autoradiographed it will be found that the impurities are not located in the thin initial rod but between this and the grown material (Figure 1). In this case, therefore, the additional use of

Table 2. Inhomogeneous distribution of impurities in high–purity polycrystalline silicon.[a]

Sample No.	Distance from rod end	Arsenic		Copper		Phosphorus		Sulphur	
		edge	center	edge	center	edge	center	edge	center
2	2 cm	2.2	0.1	0.1	3.0	4.9	38	100	5000
12	21 cm	6.5	0.3	0.4	2.4	8.7	89	91	1000
16	28 cm	8.2	0.5	0.4	2.2	5.8	55	–	–

[a] Concentration in ppb = 10^{-7} %.

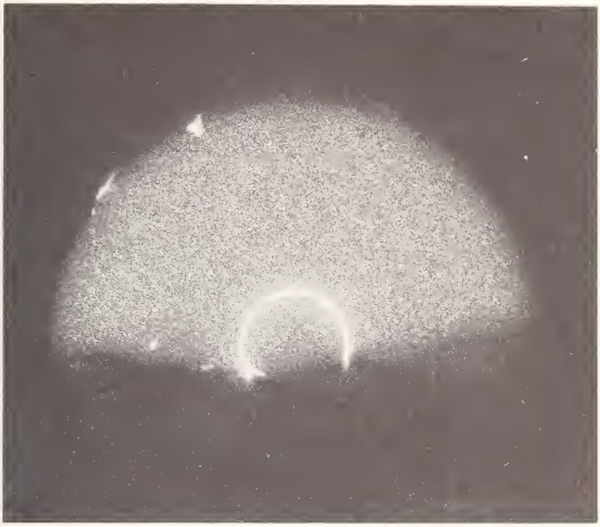


Figure 1. Autoradiograph of the cross section of half of a polycrystalline silicon rod. (Enlargement = 4:1).

simple autoradiography provides an indication of the origin and cause of the increased impurity content. If on the basis of the result the surface of the thin silicon rod is better cleaned and the process at the beginning of the growing operation slightly modified, the impurity zone disappears and the growing silicon becomes monocrystalline as shown by the autoradiography in Figure 2.

On purification and homogenizing of the semiconductor silicon by zone refining in the further course of manufacture, one could then expect to obtain a homogeneous material. However, this, for example, is contradicted by the variations found in the mercury content. In Table 3 the results of activation analysis are compared with the electrically measured data of the samples. There would appear to be no relationship of any kind, despite the fact that the higher mercury content of sample 15b (1), for example, ought theoretically to have an influence on the carrier life-time. An explanation of this can be found by studying the autoradiograph in Figure 3. This was obtained by lapping sample 15b (1) in 20 μm layers and taking an autoradiograph after each lapping operation. It can be seen that the mercury on the outer edge of the silicon rod is concentrated in a small area, a condition which explains its electrically inactive behavior.

While location is of importance in the interpretation of the analytical results in the two investigations described, autoradiography can, in favorable cases, also be used to improve the sensitivity of analysis.

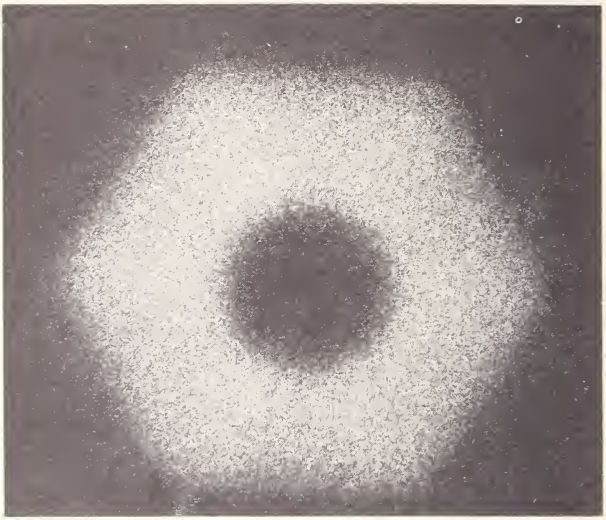


Figure 2. Autoradiograph of the cross section of a grown monocrystalline rod. (Enlargement = 4:1).

Table 3. Mercury content in zone–refined monocrystalline silicon.

Sample	Distance from rod end	Resistivity n type (Ω cm)	Carrier life time (μsec)	Hg concentration (ppb)
2	3.5 cm	114	174	3×10^{-5}
6	10.5 cm	109	435	1×10^{-3}
10	17.5 cm	105–112	725	0.11
15a	24.5 cm	107	870	0.097
15b (1)	24.5 cm	107	870	0.24
15b (2)	24.5 cm	107	870	<0.002

Example: In high purity zone-refined silicon, autoradiography with highly sensitive x-ray emulsion showed small, more exposed spots. These generally appeared against the uniformly illuminated background (Figure 4) after decay of the radiation of the ^{32}P produced from the silicon by the reaction $^{30}Si(n,\gamma)^{31}Si \xrightarrow{\beta^-} {}^{31}P(n,\gamma)^{32}P$. Autoradiographs of the sample were taken repeatedly over a period of 8 months and measured photometrically [5]. As shown by the decay curve in Figure 5, the activity in the spots decreased with a half life of approximately 80 days. Exposure with interposed aluminum foil indicated a β^- energy of 0.2 MeV. Both data match well with the nuclide ^{35}S. By comparison with

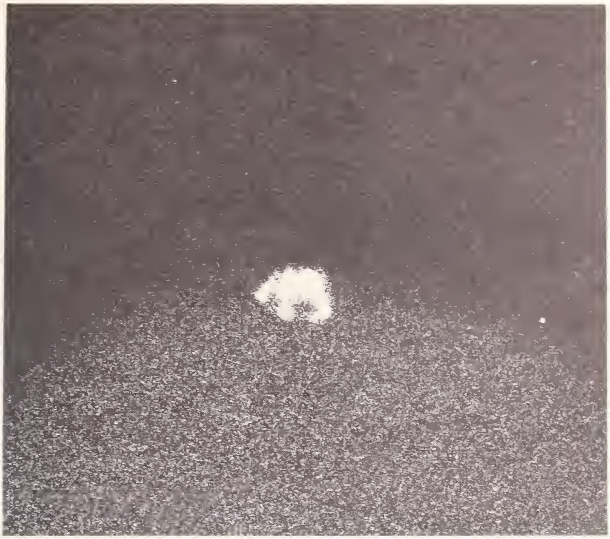


Figure 3. Autoradiograph of a disc from a zone refined monocrystalline silicon rod containing mercury.

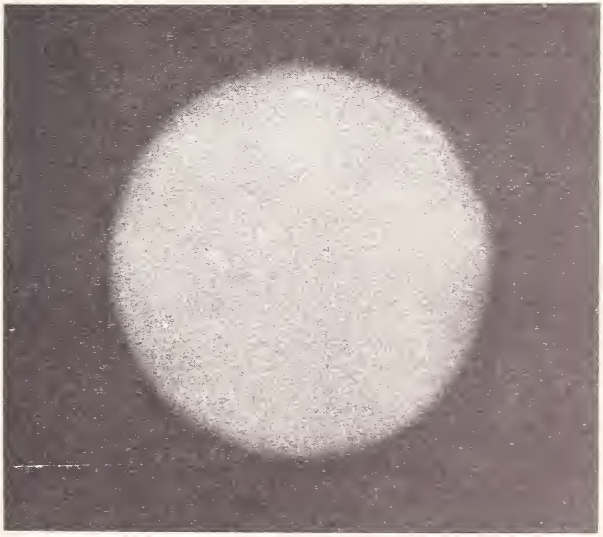


Figure 4. Autoradiograph of ^{35}S spots in zone refined monocrystalline silicon. (Enlargement = 3.5:1).

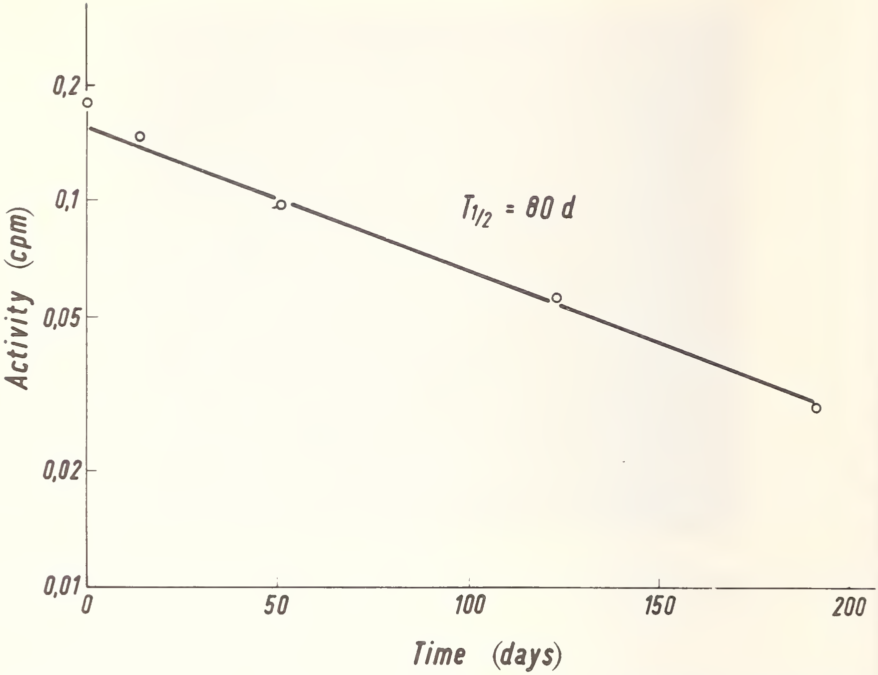


Figure 5. Decay curve of the activity in the ^{35}S spots obtained by photometric measurement of the autoradiographs.

standard exposures of the same nuclide, a quantity of 0.07 ng of sulphur was obtained per spot. Under the analysis conditions applied, the same activity could also have arisen from 0.003 ng of chlorine due to n,p-reaction. Since a sensitivity limit of 10 ng was attained for the activation analysis of sulphur under the same irradiation conditions, measurement and identification through autoradiography, although very time-consuming, produced a sensitivity of detection that was better by a factor of 100.

The following example is taken from the manufacture of semiconductor components. Diodes for the electrical equipment of automobiles rejected in an automatic sorting process during manufacture were opened and the diffused silicon square subjected to activation analysis. The main impurity found was copper which should in view of the quantity present have affected the electrical performance of the diode. Despite this, the relationships, *e.g.*, with the reverse current at 180 °C, were marked by a larger deviation range than expected. Autoradiography showed that in some silicon squares accumulations of copper occurred at the outer edge. The degree of copper accumulation was divided into 3 classes, namely, one with no inhomogeneous copper, one with a weak copper accumulation and one with a strong copper accumulation (Figure 6). If the copper content is plotted against the reverse current at 180 °C for these classes, the distribution shown in Figure 7 is obtained. According to this, the abnormal deviation range of the values is caused by the accumulation of copper at the edge of the silicon square. Expressed in solid state terms, therefore, the copper accumulated inhomogeneously at the edge has only a slight influence on the reverse current behavior of the diode at 180 °C compared with the homogeneously distributed copper.

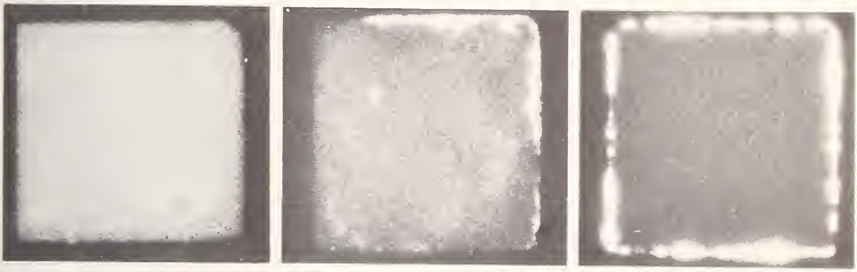


Figure 6. Autoradiographs of copper impurities on silicon diodes. (Enlargement = 10:1). Left: No accumulation at the edge; Center: Weak accumulation at the edge; Right: Strong accumulation at the edge.

The combination of activation analysis and autoradiography may find a wide field of application in the investigation of very small silicon components, such as transistors and integrated circuits. It is known that heavy metals have the undesirable effect of making the reverse characteristics soft. Analysis of the individual systems shows that the small substance quantities make the limits of sensitivity very unfavorable. A method that has proved more successful is to irradiate the diffused systems on the silicon discs before they are separated and then to localize the main activities by autoradiography before carrying out the activation analysis on etched and lapped fractions. Figure 8 shows a section (magnified 16 times) of a disc with base diodes of a transistor. The white spots are caused by gold, the quantity of which was found by activation analysis to be 1 to 5 ng per spot. In a similar manner it was, for example, possible to detect and locate the abrasion of measuring prongs on the transistor systems. Relationships to the electrical properties can then be checked simply by comparing the results with the measurement cards of the discs.

In some instances it is important to determine the diffused area in which the impurities are located. In such cases it is possible through the use of high resolution stripping film, *e.g.*, AR 10 by Kodak, to obtain

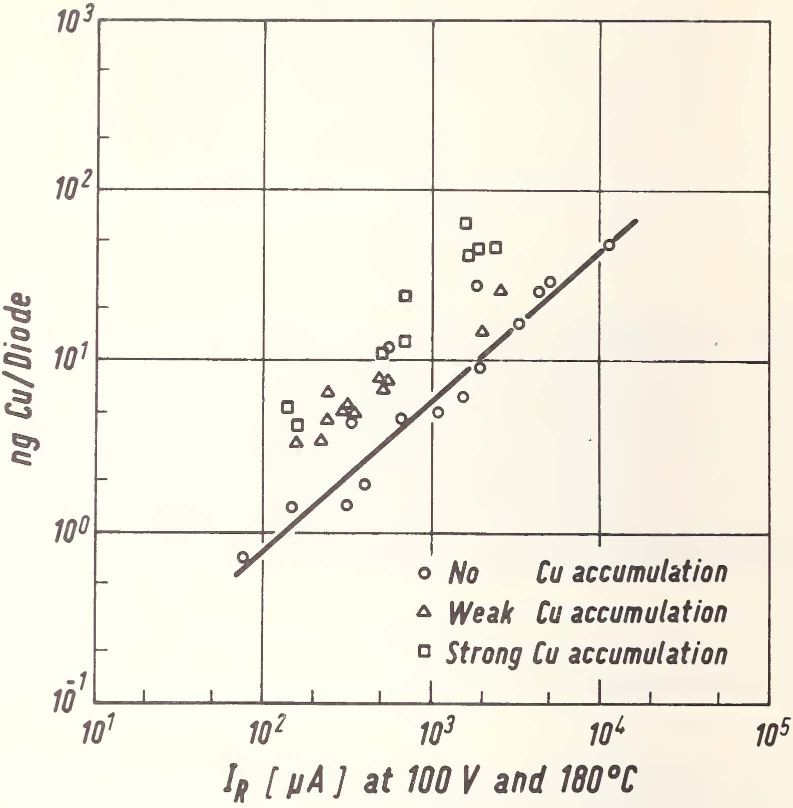


Figure 7. Relationship between copper content and reverse current at 180 °C allowing for accumulation at the edge.

enlargements of 100 to 300-fold if the autoradiographs are enlarged by microphotography. An example of this is shown in Figure 9.

Summarizing the main points of the combination of activation analysis and localization and generalizing them to include other investigations, the following can be stated:

Wherever the activity conditions of the matrix substance and the impurities permit, highly sensitive activation analysis should be combined with location of the impurities. In cases where the activity of the impurities predominates, autoradiography should be used. Where the activity of the matrix predominates, activation analyses should be combined with the chemical separation of parts separated mechanically or by etching. This should provide important indications as to the origin, behavior or mechanism of these impurities. In exceptional cases the range of activation analysis may even be extended by autoradiography. It will

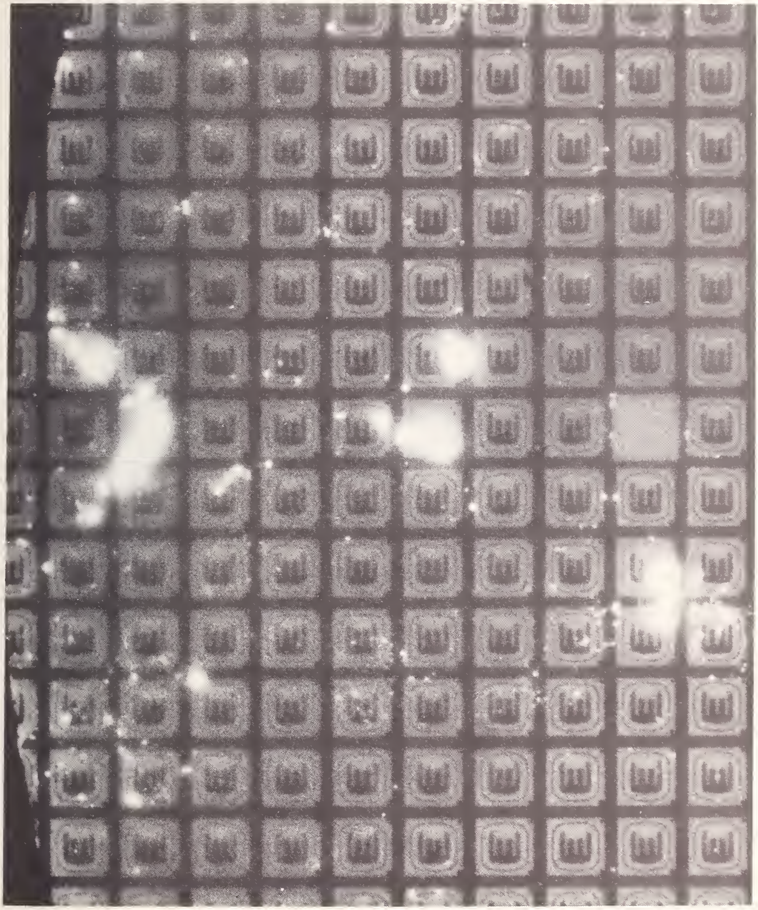


Figure 8. Section from the autoradiograph of a silicon disc with planar diodes. (Enlargement = 16:1).

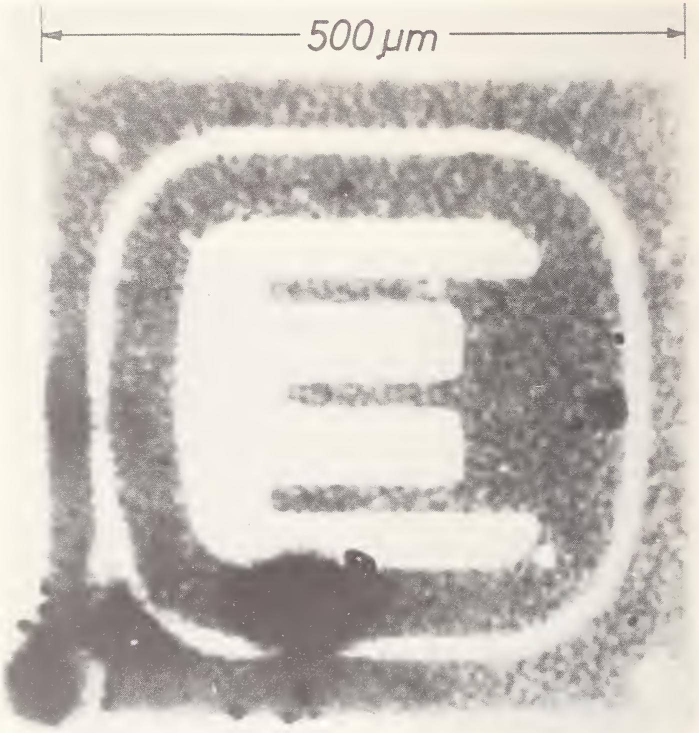


Figure 9. Microphotograph of a high resolution autoradiograph of a base diode. (Enlargement = 170:1).

also be possible in some instances to explain the absence of relationships between analysis results and the results obtained by other methods.

These findings are not restricted to the field of semiconductor analysis, but may also be of importance in the analysis of metallic alloys, reactor materials, minerals, *etc*.

IV. References

[1] Thompson, B. A., Strause, B. M., and Leboeuf, M. B., Anal. Chem. **30,** 1023 (1958).

[2] Gebauhr, W., Radiochimica Acta **4,** 191 (1965); Radiochimica Acta **5,** 8 (1966).

[3] Stevens, G. W. W., Brit. J. Radiol. **23,** 723 (1950).

[4] Osborne, J. F., Intern. J. Appl. Radiation Isotopes **18,** 829 (1967).

[5] Bishop, M., and Fletcher, K. E., Intern. J. Appl. Radiation Isotopes **18,** 465 (1967).

THE DETERMINATION OF COPPER AND GOLD TRACE IMPURITIES IN HIGH PURITY GALLIUM BY ACTIVATION ANALYSIS WITH PRETREATMENT

L. G. Nagy and G. Torok

Department of Physical Chemistry
Polytechnical University
Budapext XI, Budafoki ut 8, Hungary

L. Szokolyi

National Office of Measures
Budapest XII, Nemetvolgyi ut 37/39, Hungary

J. Giber

"Tungsram" Electric Corporation
Budapest IV, Vaci ut 77, Hungary

I. Introduction

The selection of investigative techniques suitable for gallium is subject to limitations imposed by its nuclear properties such as capture cross section for neutrons and half life. The half life of ^{72}Ga is 14.3 h being in the same order of magnitude as that of ^{64}Cu, among others. After 1-2 days of activation its activity may reach the 10 Ci/g level ($\phi = 10^{13}$ $n \cdot cm^{-2} \cdot sec^{-1}$).

The determination of isotopes with half lives of 0.1-10 days, therefore, definitely requires destructive separation [1,2] since more than 20 peaks have been identified in the 0.12-3.3 MeV region of the ^{72}Ga gamma spectrum. On the other hand the determination of trace impurities parts per million to parts per billion (ppm-ppb) requires 0.1-1.0 g gallium samples. As a consequence, samples with an activity of 1-10 Ci should be radiochemically processed, this being only possible in a hot laboratory.

Our objective was to develop a method which would be suitable for destructive activation analysis of gallium in laboratories for medium activity levels. Therefore, we had to decrease the activity of the gallium matrix by at least 2 orders of magnitude. This can be achieved by pretreating the sample before activation.

The essential feature of the method is that the concentration of the trace impurity is increased relative to that of gallium. In principle, this can be accomplished in two ways: (1) the trace impurities are separated from the material (*e.g.*, by electrochemical or chromatographic techniques); (2) the basic material is removed or its concentration decreased. Both possibilities have been tested in preliminary experiments.

Ion exchange and paper chromatography have been employed as possible means of using approach (1). The results were not satisfactory, thus supporting the assumption that the chemical properties of gallium would make (2) more suitable.

Utilizing the significant differences in volatility between gallium chloride and the chlorides of possible trace impurities, a distillation method has been developed for the removal of gallium.

II. Experimental

A. Apparatus and Reagents

Gallium was chlorinated in the apparatus shown in Figure 1. Its block diagram is given in Figure 2, the attachment is shown in Figure 3. Chlorine was prepared by oxidizing hydrochloric acid with potassium permanganate. In order to maintain the necessary flow-rate, nitrogen was introduced to raise the pressure by 500-1000 mm of Hg above atmospheric pressure. After pressure regulation, crude chlorine was bubbled through concentrated sulphuric acid (analytical grade purity—p.a.— and led into the reactor. Potassium permanganate and

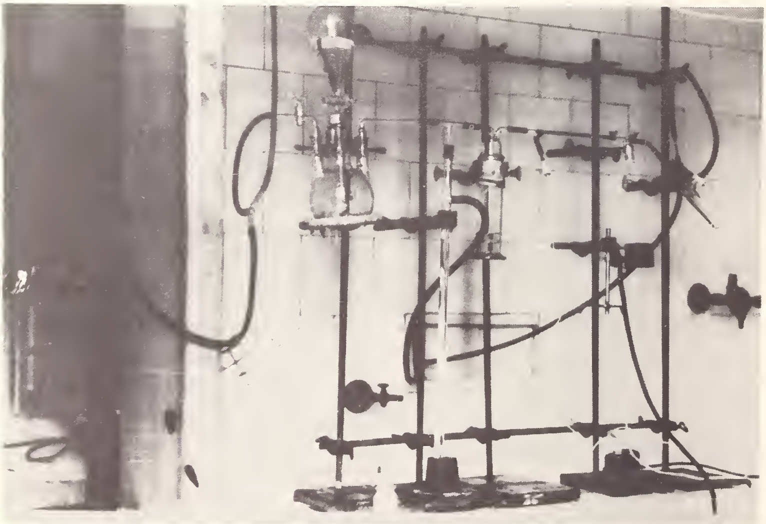


Figure 1. Photograph of chlorination apparatus.

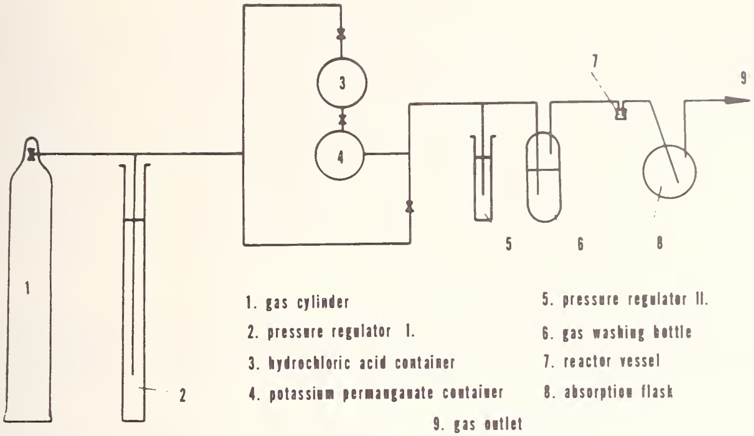


Figure 2. Block diagram of the distilling apparatus.

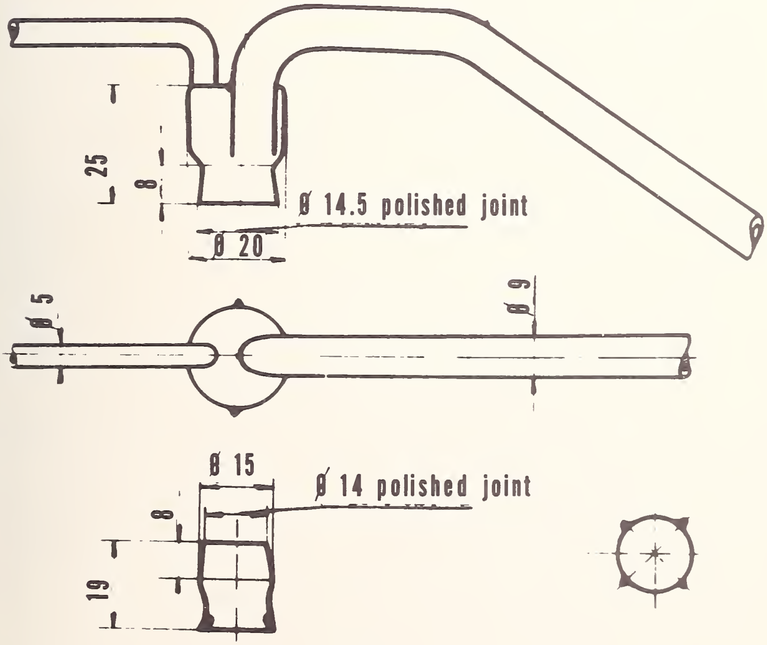


Figure 3. Reactor vessel.

hydrochloric acid (p.a., manufactured by REANAL) were used for the preparation of chlorine. The tubing that led the gas mixture in and out of the reactor was surrounded with heating spirals (Fig. 3), the distillation vial was heated with an electric hot plate. In order to avoid contamination, the distillation was carried out using the same vial in which activation was performed. The samples were activated in the reactor of the Central Research Institute for Physics, Hungarian Academy of Sciences (KFKI) with a neutron flux of (2-3) × 10^{13} $n \cdot cm^{-2} \cdot sec^{-1}$ (irradiation time 12-24 h).

Chemicals (p.a. REANAL products) were used in processing the activated samples. The cation exchange resin was of the Varion KS type (Hungarian product, H^+-form, column length 200-300 mm, diameter 8 mm, capacity 12-18 meq).

A 10-20 mg copper(II) oxide standard (spectroscopic purity) was activated with the sample in all cases. Intensities were measured with a single channel amplitude analyzer (System GAMMA Works).

B. PROCEDURE

The activation analysis of copper and gold impurities in gallium included the following steps:

1) distillation with chlorine gas prior to activation,
2) irradiation,
3) decomposition of the activated sample,
4) separation of the elements to be analyzed,
5) preparation of samples suitable for quantitative analysis,
6) intensity measurements and check of radiochemical purity,
7) preparation of a copper monitor sample and its analysis.

The apparatus was first deoxygenated by flushing with nitrogen and cold chlorine gases, for 5 minutes each. The deoxygenation determines the efficiency of the distillation procedure. Chlorination starts after the heating is begun. (Gallium trichloride boils at 201.3 °C) The reaction is exothermic, heating is only necessary to compensate for losses of heat. Gallium trichloride distills as a white smoke. (The optimum time for distillation is 20-30 min, the optimum sample weight about 100 mg).

The distillation residue (1-2 mg) had to be decomposed in the vial after activation. A suitable attachment was used during the operation. The procedure was as follows. Weighed samples (10-40 mg) of inactive copper and gold carrier solutions were added to the vial and evaporated to dryness. The dry residue was decomposed with aqua regia. After boiling off the fumes, the residue is dissolved by adding 0.1 *N* hydrochloric acid. The solution is diluted to a given volume, and aliquots are transferred to an ion exchange column. Elution with 0.1 *N* hydrochloric acid yields the gold while the copper is obtained by elution with 1.1 *N* HCl. Gold is precipitated by reduction with zinc powder [3] (in 1:1 hydrochloric acid, yield 90-95%). Copper is precipitated as copper(I) iodide [4] in a slightly acidic medium (yield 85-90%). The copper and gold contents were determined by the modified Covell-method [5], measuring the intensities, in the ranges of 0.5 and 0.4 MeV, respectively.

III. Results and Discussion

A. RESULTS

In order to establish the random and systematic errors of the method, the distillation and decomposition steps had to be subjected to a more thorough study since the losses in subsequent steps can be taken into account on the basis of the yields.

It has been observed that no contamination occurred when empty quartz vials were chlorinated under the above mentioned conditions, indicating that the chlorine did not contain impurities which would condense and become radioactive in the vial.

The efficiency of the distillation was characterized by the percentages of the ^{64}Cu standard (η_a) and the gallium sample (η_s) in the residue.

The values of η_s·and η_a were determined by weighing, and from the number of counts, respectively. The minimum number of counts was 10^3, usually being above 10^4. The standard deviation of the intensity measurements was less than 3%, but usually did not exceed 1%.

Since copper is one of the most harmful impurities in semiconductor materials, the objective was, among others, the determination of copper.

The efficiency of distillation was studied also with ^{64}Cu because of its favorable chemical and nuclear properties.

The relatively high vapor pressure of copper halides supports the assumption that if no copper losses are observed, no losses due to evaporation of less volatile metal halides are to be expected. This has been experimentally demonstrated on the model of ^{198}Au. Since the vapor pressure of copper(II) chloride is less than 0.1 mm of Hg even at 500 °C, there is no danger of losses due to evaporation around 100 °C. (Some references quote a high value for the vapor pressure but this is the equilibrium pressure of chlorine formed in the decomposition).

The results are shown in Figures 4 and 5 as distribution curves (histograms). Figure 4 shows the results of a series where the volume of the distillation vial was around 3 ml. The diagram indicates normal distribution: $\eta_s = (80 \pm 20)\%$, and $(80 \pm 10)\%$, with 80 and 60% statistical occurrence, respectively.

Similar histograms can be constructed from the η_s data. The distillation residue is $(2 \pm 2)\%$ with 84% probability.

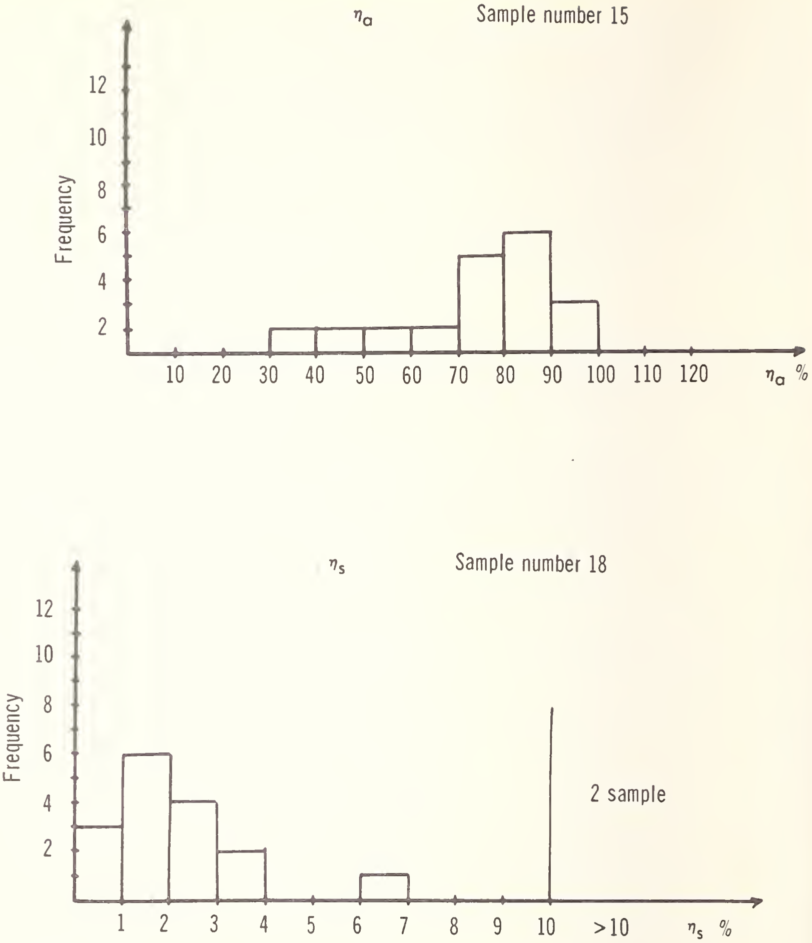
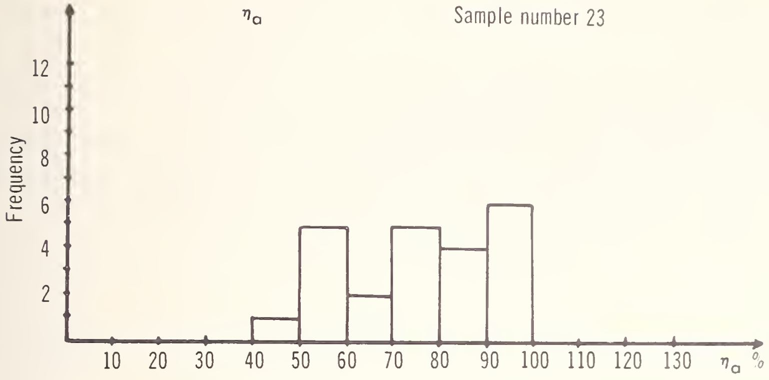


Figure 4. Frequency distribution of the first series.

Since the weight of the sample before and after distillation can be determined, samples with high errors can be discarded. Therefore, this value only serves the purpose of comparison.

Similar tests were carried out using vials of 1 ml volume, Figure 5. It can be seen, that the volume reduction of the vial modified the shape of the curve, altered the deviation. On the basis of the histogram, an accurate distribution cannot be determined, but at the same time the most probable value, the limit of error and the statistical confidence level easily can be established: (75 ± 25)% (96%) and (80 ± 20)% (74%), respectively.

In order to clarify the reasons for results at variance with the theory, intensities have been measured for a number of samples before and after



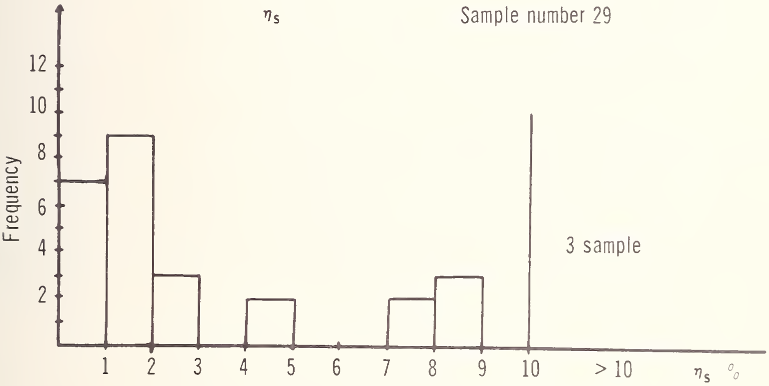


Figure 5. Frequency distribution of the second series.

chlorination, and every half hour at constant temperature and chlorine flow.

The maximum total time of chlorination was 3 h. No significant intensity changes were observed after the initial decrease at the given conditions for distillation.

Accordingly, the copper losses are due to technological factors such as carry-over, local overheating, *etc*. The characteristics and operation of the apparatus are, therefore, of fundamental importance with respect to reproducibility.

The efficiency of decomposition has also been studied with ^{64}Cu. (A sample contaminated with copper of known activity was decomposed). In the presence of 20-80 mg of copper carried, 90% of the total amount of copper has been recovered from the original vessel, the largest deviation being ±8%.

After the above data had been determined, a pure (B) and an impure (A) gallium sample were subjected to activation.

The results are shown in Table 1. The average copper contents are 2.1×10^{-6} g ± 40%, and 6.3×10^{-7} g ± 45%, while the average gold contents equal 4.3×10^{-8} g ± 50%, and 3.7×10^{-9} g ± 45%, respectively.

Table 1. Copper and gold contents of some gallium samples.

No.	Sample designation	Copper content (g/g)	Gold content (g/g)
1	A[a]	3.1×10^{-6}	
2	A	1.5×10^{-6}	6.5×10^{-8}
3	A	2.6×10^{-6}	4.5×10^{-8}
4	A	1.3×10^{-6}	2.1×10^{-8}
5	B[b]	5.2×10^{-7}	2.2×10^{-9}
6	B	9.8×10^{-7}	4.6×10^{-9}
7	B	4.0×10^{-7}	6.1×10^{-9}

[a] A = impure

[b] B = pure

B. DISCUSSION

It can be established from the distillation results that the method is suitable for purposes of activation analysis because the gallium content can be decreased by 2 orders of magnitude. However, a certain percentage of the impurites to be analyzed remains in the residue. The pretreatment does not contaminate the samples.

Although, in principle, 100% of the impurities should be in the residue, the experimentally observed efficiency was significantly less than 100%. According to the experimental results, the amount of copper in the residue is governed by "technological" factors.

In view of the fact that the dimensions of the irradiation channel determine the vial dimensions, the deviation can only be decreased by careful stabilization of the distillation parameters.

This statement receives support from the data in Figures 4 and 5, indicating that the efficiency is decreased and the deviation increased when the cell dimensions are decreased.

The enrichment factor $\eta_a/\eta_s = 50$ for the distillation process, *i.e.* there is no way to simplify the operations subsequent to activation. However, the original objective was not this but the decreasing of the activity level which has been achieved, the residual activity being 10-20 mCi. (The enrichment factor can only be increased by improving the distillation procedure and by a more complete deoxygenation of the system and the chlorine gas).

Since the enrichment factor for the ion exchange operation is 11 ± 3, the total radiochemical purity ratio is 1:550. (A cation exchange resin has been used because the separation of copper and gallium chloride complexes is difficult on an anion exchange resin). In agreement with the conclusions drawn from gamma spectra, this indicates the necessity to separate the impurities under consideration when a quantitative analysis is to be performed.

According to the results, the error of copper determination is $\pm 40\%$ in the range of $10^{-6}-10^{-7}$ g/g. In the case of gold the error is $\pm 50\%$ in the range of $10^{-8}-10^{-9}$ g/g (*cf.* Table 1). This indicates that the deviation of the results is practically determined by the deviation characteristic for the distillation. The latter does not exceed the error limits for activation analysis.

IV. References

[1] Nagy, L. G., *et al*, Periodica Polytechnica 7, 147 (1963).

[2] Lewis, J. E., The Radiochemistry of Aluminum and Gallium (NAS-NS 3032).

[3] Bujdoso, E., and Miskei, M., Kohaszati Lapok **99**, 281 (1966).

[4] Erdey, L., Gravimetric Methods of Chemical Analysis, Vol. II, p. 110, Publishing House of the Hungarian Academy of Sciences, Budapest, 1960.

[5] F. Csanyi, P., Gallyas, M., and Levay, B., Magyar Kem. Folyoirat 71, 127,234 (1965).

NEUTRON ACTIVATION ANALYSIS OF LASER CRYSTALS

Ruben F. Ortega [1]

Department of Chemical Engineering,
Imperial College of Science and Technology,
London, England

I. Introduction

A great deal of effort has been devoted in the last few years by the group on "New Laser Crystals" of Imperial College, to the production of new test materials in the field of electro-engineering research. With the help of new growth techniques [1], crystals of the highest lattice perfection are obtained as hosts of paramagnetic impurities. A relevant example of interest for laser applications is flux growth, stoichiometric spinel, doped with small quantities of a particular ion, *i.e.* $MgAl_2O_4$:Cr which presents similarities with ruby crystals (Al_2O_3:Cr). A survey of known spinel structures had indicated the possibility of incorporating a number of ions, and there was particular interest to know the possibility of incorporating the smaller rare earth elements; since the flux growth process provides an advantageous means of doping the crystals, maintaining a reasonable concentration of dopant during growth.

The spinel crystals were grown from solution in lead fluoride by isothermal evaporation between 1200 and 1250 °C in partially sealed 100 ml platinum crucibles. Specially prepared high purity magnesia and alumina were provided by British Drug Houses Limited and a high purity grade of lead fluoride obtained from Associated Lead Company Limited was used as solvent.

Erbium or neodymium oxides were added in various proportions to the initial mixture, but even at relatively high initial concentration (approximately 5 mol %), name of the rare earth additives was detectable by conventional analytical methods as absorption spectroscopy. At slow growth rates (less than 1 mm/day linear), the $MgAl_2O_4$ spinel crystals were remarkably free from inclusions detectable by light scattering, and previous analysis of such crystals have shown to have a lead content of less than 10 parts per million. But no other information about the purity of the crystal was known, especially contamination with crucible (platinum, rhodium, iridium) or solvent (manganese, antimony) elements.

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[1] Present address: Centro Nuclear de Mexico, Mexico City, Mexico.

Neutron activation analysis potentially provides an unambiguous, absolute method for the determination of very small concentrations of dopant, and for this particular case provided unexpected additional information on trace impurities of relevance to the physical studies being undertaken on these crystals.

II. Experimental

A. IRRADIATION AND COUNTING

Crystal specimens of 50 to 100 mg were selected and cleaned by immersion in boiling phosphoric acid for ten minutes. These were packed in small, precleaned polyethelene containers and loaded with the standards into the core of the University of London Nuclear Reactor, by means of a pneumatic system, to be irradiated at full reactor power (thermal neutron flux of $1.5 \times 10^{12} n \cdot cm^{-2} \cdot sec^{-1}$) for two hours.

After irradiation the samples and standards were allowed to "cool down" for up to one day, to allow the activity of the matrix elements to decay. They were then counted in a gamma-ray analyzer system consisting of a 3 in. × 3 in. thallium doped sodium iodide crystal coupled to a photomultiplier tube and a multichannel analyzer "Intertechnique" SA 40B.

The method of "least squares" [2] was applied in the evaluation of the results for the resolution of the spectrum of the crystal. Two typical computer codes [3,4] were used for the processing of the data. In the case of erbium analysis, the crystal was counted after 30 minutes "cooling" to determine the 7.5 h ^{171}Er formed. Standards of erbium, magnesium and iridium were used as linear components of the crystal spectrum. A problem of interference was presented by the 0.32 MeV peak of the 74 day ^{192}Ir on the 0.305 MeV peak of ^{171}Er. However this peak can be easily resolved by using a lithium drifted germanium detector. A comparison of the spectra of a doped crystal, an undoped crystal and an erbium standard is shown in Figure 1.

The analysis of neodymium was made on the 0.21 MeV peak of the 1.9 h ^{151}Nd, but could also be made on the decay product 28.4 h ^{151}Pm. For the iridium and sodium analysis, the crystal was counted after a "cooling" period of one day and the 0.32 MeV peak of ^{192}Ir and 1.37 MeV peak of the 15 h ^{24}Na were measured by using a compound spectrum of erbium, sodium and iridium in the fit.

B. STANDARDS

For the determination of rare earth elements a standard solution of about 10 μg/ml of the element was prepared by dissolving the oxide in 0.1

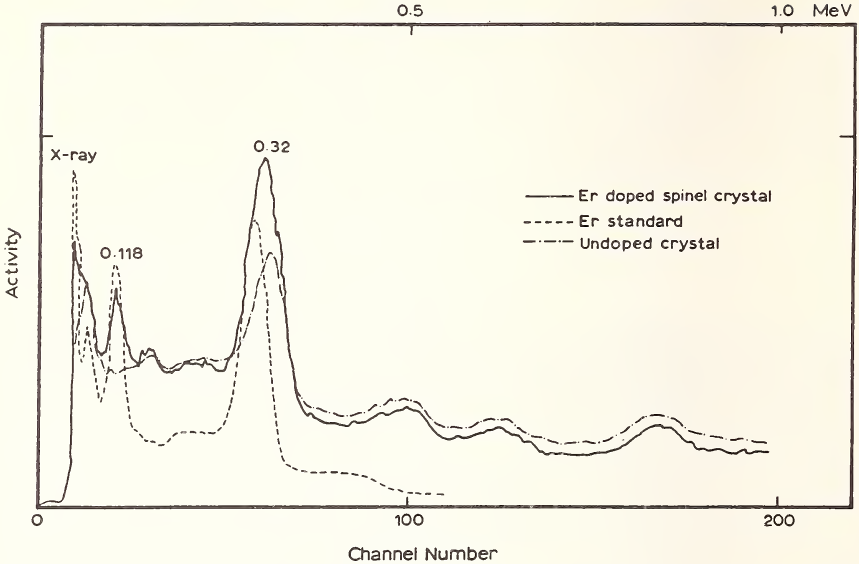

Figure 1. Comparative spectra of erbium standard, erbium doped crystal and undoped crystal.

N nitric acid. From this solution fractions of ml were pipeted and dried into a clean polyethelene container.

For the determination of iridium a standard solution of ammonium chlororidate $(NH_4)_2IrCl_6$ in 0.1 *N* hydrochloric acid was prepared. For sodium a standard solution of sodium hydroxide was used. Both solutions were in the concentration range of 20 to 40 μg/ml in the sought element. A calibration of the standard procedure is shown in Figure 2.

III. Results

The result from one analysis is given in Table 1. The error involved in these figures is about 1% in the standard procedure and less than 3% in the counting and evaluation of the results.

The presence of iridium in all of the crystals examined was surprising. This attributed to the dissolution of iridium present as an impurity in the platinum crucibles into the solvent with subsequent incorporation in the crystal. The evidence of iridium contamination in the crystals was confirmed by the activation analysis group of Dr. D. Gibbons at Wantage Nuclear Laboratories in the analysis of similar crystals doped with chromium.

The sodium recorded is the one produced by fast neutron reactions on the matrix. Evidence of other elements such as platinum, chromium, manganese and antimony was found, but these were not present in

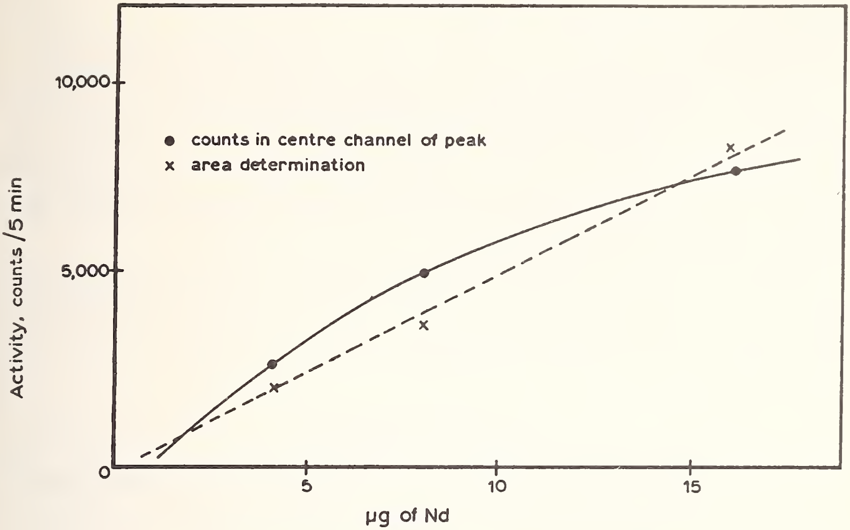

Figure 2. Standard calibration curve for neodymium analysis.

Table 1. Result of one analysis.

Element	Concentration (μg)
Rare earth (Er)	0.0524
Iridium	0.0133
Sodium	0.1652

significant amounts in the crystals. For detection of elements such as fluorine or silicon, fast neutron irradiation with 14 MeV neutron generators is advisable [5].

IV. Discussion

A nondestructive technique of analysis was used for the determination of the rare earth elements, iridium and sodium in stoichiometric spinel "laser" crystals by allowing optimum time of irradiation and decay [6], gamma-ray spectrometry and treatment of the data in fast computers (IBM 7090). A FORTRAN IV computer program was developed for the resolution of the gamma-ray spectrum of the crystal by using a linear "least squares" technique.

The results have shown that the smaller rare earth ion Er^{3+} can be incorporated in the lattice of the crystal to a small extent, but the larger Nd^{3+} ion is rejected. Contamination of the crystal with iridium was disclosed. This impurity is derived from iridium in the platinum crucibles used to contain the melts at high temperatures. No evidence of similar platinum contamination was found.

In general, it was possible to develop a simple and accurate activation analysis for qualitative and quantitative determinations in the crystals. This can be of great help in the interpretation and physical measurements and for the control of crystal growing.

V. Acknowledgments

Thanks are due to Professor G. R. Hall for his encouragement and to the staff of the University of London Reactor for their assistance.

I also want to thank the International Atomic Energy Agency for a fellowship and the Mexican Atomic Energy Commission for a grant.

VI. References

[1] White, E. A. D., Tech. of Inorganic Chem. **4**, 31 (1964).
[2] Salmon, L., NAS-NS 3107, 165 (1963).
[3] Schonfeld, E., ORNL-3810 (1965).
[4] Murphy, H. M., Jr., AFWL-TR-65-111 (1966).
[5] Coleman, R. F., Analyst **86**, 39 (1961).
[6] Isenhour, T. L., Evans, C. A., Jr., and Morrison, G. H., Proceedings 1965 Int. Conf. "Modern Trends in Activation Analysis", 123 (1965).

DETERMINATION OF TRACES OF SELENIUM AND TELLURIUM IN SULPHUR BY NEUTRON ACTIVATION

A. Arroyo A. and J. Toro G.

Instito de Asuntos Nucleares
Bogota, D.E., Colombia

I. Introduction

This work has been done in order to give a method for the determination of traces of selenium and tellurium in sulphur by activation of the samples with thermal neutrons produced in the IAN-Rl reactor.

The determination of the elements, selenium and tellurium, that are found associated with native sulphur is very important because their occurrence affects the quality of the products that use sulphur as prime material. Furthermore, because of their toxicity, it has been necessary to control their presence in fertilizers, drugs, detergents, moistening agents, *etc.* The effects of the selenium in cattle fed with grass grown in soils that contain selenium are widely known.

On the other hand, the content of these elements in native sulphur is generally less than 1% and it is necessary to get an analytical method with high sensitivity. The determination by chemical and spectrometric methods offer many difficulities, especially with native sulphur because they are elements located in the same group of the periodic chart of the elements with similar chemical and physical properties. The method developed and presented in this work is expected to resolve this problem satisfactorily.

II. Experimental

The method is based on the fact that when a stable isotope is irradiated by neutrons it can undergo a nuclear transformation to produce a radioactive nuclide. The irradiations were done in the pneumatic tube system of the reactor in a flux of 10^{11} $n \cdot cm^{-2} \cdot sec^{-1}$. The samples of sulphur were irradiated in paraffin matrices of confirmed purity and constant geometry in all of the samples. They were taken in quantities of the order of a tenth of a gram.

^{77m}Se and ^{131}Te radionuclides were selected as the most appropriate isotopes to be followed in the determination because they give a clear spectrum that facilitates the analysis and eliminates the difficult radiochemical separation (see Figures 1 and 2). The samples after irradiation were counted in a 511 channel pulse analyzer coupled to 2 in. × 2 in. NaI(Tl) detector. The quantitative results were obtained by comparison of photopeak areas with those of the standards. Standards were prepared with homogeneous mixtures of different composition with reactive sulphur, sodium biselenite, metallic selenium, potassium tellurite and metallic tellurium.

III. Results and Discussion

The method described gives a detection sensitivity of 0.07 micrograms of selenium and tellurium in the presence of sulphur with a great economy of time compared to other analytical methods, and it gives sufficient accuracy. The samples were not submitted to any chemical treatment before or after irradiation. The tests were repeated on several samples that had the same amount of selenium and tellurium, and the results have shown that the method is consistent, that is, the obtained data can be repeated within 1% of deviation.

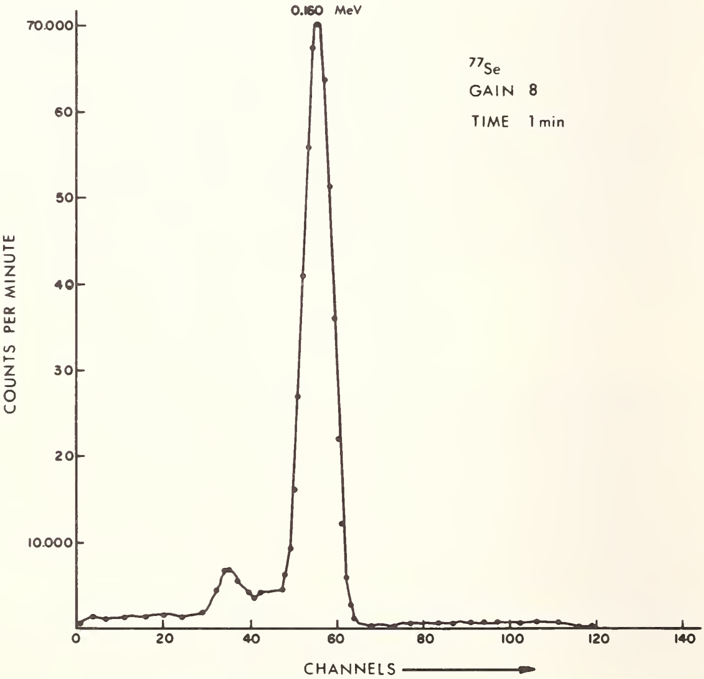

Figure 1. Gamma-ray spectrum of ^{77}Se.

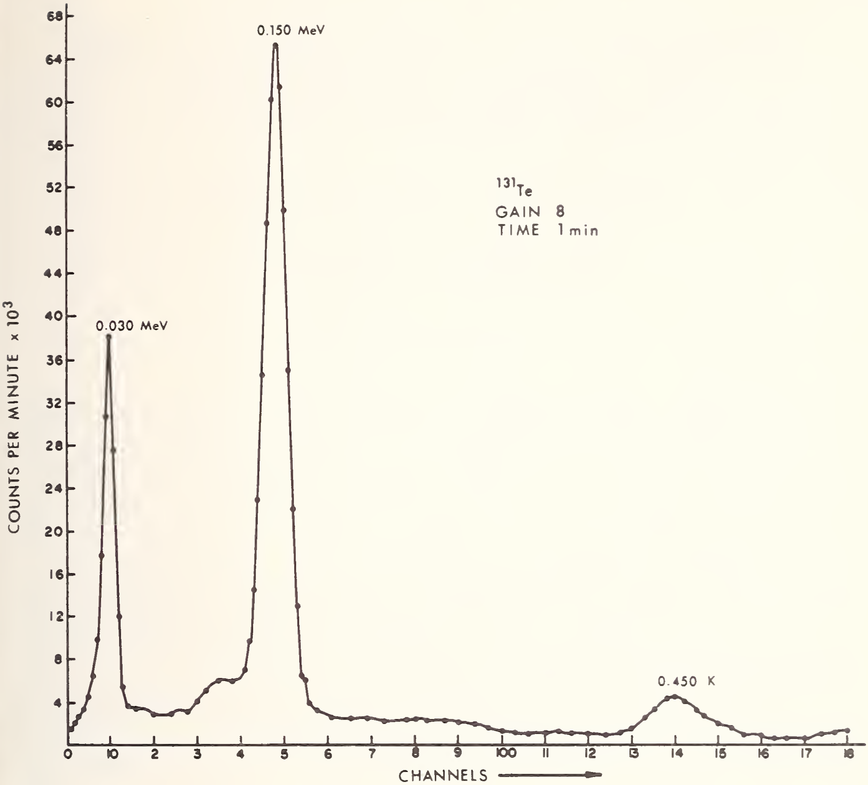

Figure 2. Gamma-ray spectrum of ^{131}Te.

IV. References

[1] Review of Modern Physics **30**, part 2 (1958).

[2] Dzhelepov, B. S., and Peker, L. K., "Decay Schemes of Radioactive Nuclei", Pergamon Press, London, 1961.

[3] Sandoval, E., Barragan, A., and Casabianca, M., "Guia General Parra Irradiaciones en el Reactor de Ensenanca e Investigacion", IAN-R1, Instituto de Asuntos Nucleares, Colombia, 1965.

[4] Dana, J. D., and Dana, E. S., "The System of Mineralology", John Wiley & Sons, New York, 1957.

NONDESTRUCTIVE ACTIVATION ANALYSIS FOR ARSENIC AND ANTIMONY IN SOFT SOLDERING ALLOYS

M. D. Rudelli, H. C. Rocca and G. B. Baro

Comision Nacional de Energia Atomica
Departamento Aplicacion (G.E.)
Buenos Aires, Argentina

I. Introduction

Many elements and matrices have already been examined by nuclear activation analysis; such a technique is now well established. Little work has been done, however, on the activation determination of impurities in tin or its compounds. The authors are aware of only two publications [1,2].

In the activation analysis of antimony in pure tin or high tin matrix, a problem arises from the contribution to the antimony content by the matrix, even when chemical separation has been conducted. This is due to the presence of ^{125}Sb produced by the reaction $^{124}\mathrm{Sn}(n,\gamma)^{125}\mathrm{Sn} \xrightarrow{\beta-} {}^{125}\mathrm{Sb}$. From published nuclear data (Tables 1 and 2) we find that the energy of the gamma rays of ^{125}Sb is quite similar to the energy of the gamma rays of ^{122}Sb and ^{124}Sb, both produced by n,γ reaction from natural antimony. They are within the resolution of the best NaI(Tl) crystals.

Previously this situation was overcome [3] by counting both the irradiated sample and a standard with a NaI(Tl) detector, each of them twice. The first count was made after a reasonable cooling period (3 days) and the second one when most of the ^{122}Sb would have decayed.

Table 1. Nuclear properties of antimony and arsenic isotopes.

Stable isotope	Occurrence (%)	Activation cross section (barn)	Isotope formed	Half life	Gamma energy (keV)
^{121}Sb	57.25	6.8	^{122}Sb	2.75 d	564; 686; 1137; 1258
^{123}Sb	42.75	2.5	^{124}Sb	60.9 d	603; 646; 723 1692; 2088
^{75}As	100.0	5.4	^{76}As	26.3 d	559; 657; 1216

Table 2. Interfering activities from the matrix.

Stable isotope	Occurrence (%)	Activation cross section (barn)	Isotope formed	Half life	Gamma energy (keV)
^{112}Sn	0.96	1.3	^{113}Sn	115 d	260; 392
^{116}Sn	14.30	0.006	^{117}Sn	14 d	320
^{122}Sn	4.72	0.16	^{123}Sn	41 m	153
		0.001	^{123m}Sn	131 d	1080
^{124}Sn	5.94	0.2	^{125m}Sn	9.5 m	326
		0.004	^{125}Sn	9.4 d	810; 1070; 1960
			^{125}Sb	2.0 y	35; 176; 427 462; 598; 604 633

However, most of the ^{124}Sb and nearly all of the ^{125}Sb activity would remain. From counts obtained at different times, the matrix contribution can be worked out. The antimony content was computed before from the height of the 564 keV peak of ^{122}Sb.

The presence of arsenic, however, causes a serious interference because of the photopeak of ^{76}As at an energy of 559 keV which cannot be resolved from the 564 keV peak of ^{122}Sb. Since arsenic is a common contaminant, it appeared desirable to develop a gamma spectrometric activation analysis for the two elements.

Because the activation cross sections of the natural lead isotopes ^{206}Pb and ^{208}Pb are very small (0.026 and 0.0006 barn), the activity induced in the other major constituent of the matrix is quite negligible.

A number of other elements occurring either as minor constituents or as traces might, however, interfere with both the arsenic and antimony determinations. The nuclear properties of possible trace elements in the alloys such as copper, iron, zinc, silver and sodium, are shown in Table 3. A number of isotopes are produced from these elements and have half lives considerably smaller than ^{76}As and ^{122}Sb. Their interference can be minimized by choosing an optimum cooling time. Moreover, if the irradiation time is short, the activities from the longer-lived species ^{65}Zn and ^{110m}Ag will also be negligible. Still, with the technique to be described, the only actual interference from the gamma spectroscopy point of view should be ^{110m}Ag. The others will contribute to the background.

At present the best way to deal with the above stated problems is to use lithium drifted germanium detectors. It is possible with them to distinguish gamma rays differing in energy as little as 2-4 keV in complex gamma-ray spectra, and to determine their absolute energy to better than

Table 3. Interfering activities.

Stable isotope	Occurrence (%)	Activation cross section (barn)	Isotope formed	Half life	Gamma energy (keV)
^{63}Cu	69.1	4.51	^{64}Cu	12.8 h	511; 1340
^{64}Zn	48.9	0.47	^{65}Zn	245 d	511; 1119
^{68}Zn	18.57	0.097	^{69m}Zn	13.8 h	438
^{109}Ag	48.65	3.2	^{110m}Ag	253 d	655; 685; 706 760; 884; 935 1386
^{58}Fe	0.33	1.01	^{59}Fe	45.1 d	1100; 1290
^{23}Na	100.0	0.54	^{24}Na	15 h	1375; 2760

0.5 keV. Because of their high resolution, individual photopeaks stand out more distinctly over background radiation. In this way it is possible to detect relatively weaker gamma lines in a spectrum, than if scintillation detectors were used.

II. Experimental

The detector used was a 5 cm^3 planar type Ge(Li). The associated electronics consisted of a low noise preamplifier, a main amplifier and a biased amplifier, all of them designed and assembled by the Instrumentation Department (CNEA). Pulse-height analysis was done with a Model 130A Nuclear Data multichannel analyzer.

Two sets of samples were analyzed; the first one was artificially prepared. "Specpure" metallic tin was digested in p.a. nitric acid, and then known amounts of arsenic and antimony were added. Afterwards, they were dried to constant weight and thoroughly mixed. The second set consisted of commercial samples of soft soldering alloys, with different tin content.

The samples (0.1 to 0.3 g) and standards, packaged or sealed in polyethylene vials, were irradiated in the RA.1 reactor at a flux of 10^{12} $n \cdot cm^{-2} \cdot sec^{-1}$ for 8 hrs. Afterwards, they were allowed to cool for 24 hrs. before counting.

In order to get an accurate measure of the peak areas, the biased amplifier was used to expand the spectrum above 470 keV. The final setting gave a channel width of 0.75 keV/channel. The system had a resolution (FWHM) of 5.2 keV for 657 keV. To avoid distortion of the photopeaks due to a bad response of the amplifier towards moderately high counting rates, a high Z material (lead) was used to shield the detector.

The optimum counting time was 100 minutes per sample, but unfortunately this was not possible with all the samples. The antimony content was computed from the activity in the 686 keV photopeak of ^{122}Sb, and that of arsenic from the 657 keV peak of ^{76}As, according to Covell [4] (Figs. 1 and 2).

III. Results

The results of a number of analyses for concentration of antimony and arsenic are summarized in Table 4. Table 5 gives the results of a number of analyses for arsenic and antimony in commercial soft soldering alloys. In one of the samples, due to its high antimony content, arsenic was not detectable. As shown, standard deviations are generally better than 10%.

It is evident that use of larger detectors and faster electronics will improve both accuracy and sensitivity.

With the above described work, it may be concluded that the limitations for the nondestructive activation analysis of both arsenic and antimony in a tin matrix are alleviated by the use of Ge(Li) spectrometers.

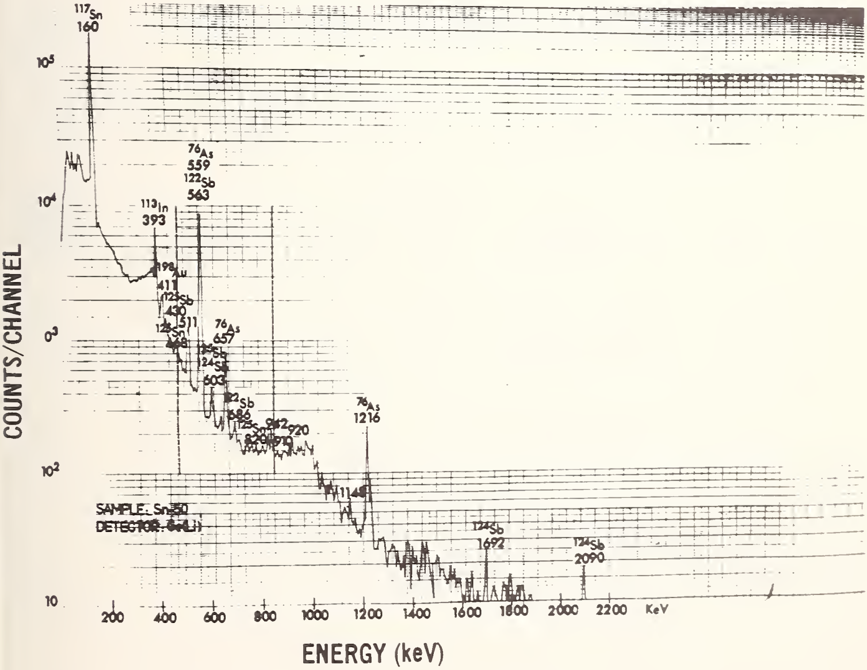

Figure 1. Alloy sample Ge(Li) spectrum.

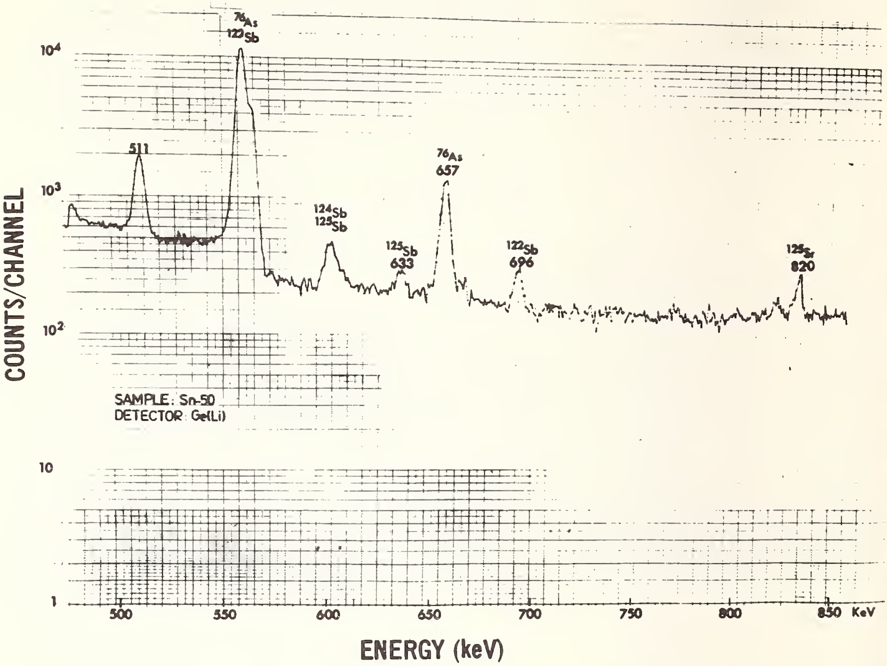

Figure 2. Biased spectrum alloy sample.

Table 4. Activation analysis of tin samples.

Sample	Sb taken	Sb found (average)	Number determined	As taken	As found (average)	Number determined
1	62.34[a]	62.3 ± 9.7[a] S = 15.56%	6	10.57[a]	12.4 ± 1.4[a] S = 11.29%	5
2	40.65	41.2 ± 2.4 S = 5.82%	5	39.39	40.4 ± 3.0 S = 7.42%	4
3	8.85	12.3 ± 1.5 S = 12.20%	2	5.05	6.2 ± 0.3 S = 4.82%	3
4	12.93	12.5 ± 0.8 S = 6.56%	8	5.00	5.4 ± 0.7 S = 12.40%	6

Table 4. Activation analysis of tin samples. (continued)

Sample	Sb taken	Sb found (average)	Number determined	As taken	As found (average)	Number determined
5	0.0586[b]	0.0553 ± 0.0076[b] S = 13.74%	4	0.0026[b]	0.0027 ± 0.0003[b] S = 11.11%	3
6	0.319	0.281 ± 0.032 S = 11.38%	4	0.0033	0.0025 ± 0.0002 S = 8.0%	2

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[a] Value in parts per million.

[b] Value in percent.

Table 5. Activation analysis of soft soldering alloys.

Sample	Sb found (average)	Number of determinations	As found (average)	Number of determinations
NL 1 (Sn 33)	36.4 ± 4.2[a] S = 11.54%	7	72.1 ± 5.5[a] S = 7.62%	8
NL 2 (Sn 40)	39.1 ± 4.1 S = 10.48%	8	63.2 ± 4.0 S = 6.32%	9
NL 3 (Sn 50)	50.1 ± 4.5 S = 8.98%	8	82.1 ± 4.9 S = 5.96%	9
NL 4 (Sn 60)	56.9 ± 5.1 S = 8.96%	5	95.2 ± 4.7 S = 4.93%	6
In 1 (Sn 33)	0.744 ± 0.079[b] S = 10.61%	5	Not detectable	5

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[a] Value in parts per million.

[b] Value in percent.

IV. References

[1] Leddicotte, G. W., Proc. 2nd Inter. Conf. Peaceful Uses At. Energy, United Nations, Geneva **28,** 478 (1958).

[2] Rauscher, H. E., Anal. Chem. **38,** 519 (1966).

[3] Simpson, H., Personal communication.

[4] Covell, D. F., Anal. Chem. **31,** 1785 (1959).

THE APPLICATION OF THE ACTIVATION ANALYSIS TO THE INVESTIGATION OF SORPTION AND SUBLIMINATION PROPERTIES OF HIGH-TEMPERATURE MATERIALS

I. A. Maslov, V. A. Lucknitsky, N. M. Karnauckova, and G. I. Karajanova

Ioffe Physico-Technical Institute
Academy of Sciences
Leningrad, USSR

I. Introduction

Activation analysis (AA) is a very useful method for investigation of physical, chemical and technological processes which are accompanied by the displacement of small amounts of substance. In comparison with the "marked atoms" method traditionally used in these problems the application of AA is more expedient for two reasons:

1. The real materials are used as the objects of the experiment; therefore, their properties are not distorted by the presence of the "mark".
2. The experiment is carried out in the usual laboratory conditions, and only the final state of the quantitative control is made in a special radiochemical laboratory.

As well as in the first works using the "marked atoms" the application of the AA under consideration is connected with the diffusion problems [1,2] and with the measurement of the evaporation rate of substances in vacuum [3-6].

In the present paper the special problems of the sorption and sublimation properties of high-temperature substances using neutron AA are considered and some results are given.

II. The Investigation of the Cesium Vapor Absorption by Electroinsulating Ceramics

Ceramics of the $Al_2O_3 + 1\%\ Y_2O_3$ composition has found a wide application as an electrical insulator operating at high temperatures. The operating time of the electrovacuum devices in which the cesium vapor is used is larger the less is cesium absorbed by ceramics. Therefore, it has been of practical interest to develop the method enabling, first of all, to determine with high sensitivity the total amount of cesium absorbed by 1 cm^2 of the ceramic surface, and, secondly, to give the estimate of the cesium pentration depth in the insulator.

The samples under investigation were rings, 10 g weight, 13 mm height, about 20 mm internal diameter, and about 25 mm external diameter. After the rings had been treated in the cesium vapor and their surface had been cleaned from the unabsorbed metal, they were cut into 8 sectors; each one in its turn was cut into 3 parts and the middle part was taken as a sample. Six sectors were used for neutron activation determination of the absorbed amount of cesium and its penetration depth, and the other two were sent for optico-metallographic investigation.

The estimate of the cesium determination sensitivity for average activation conditions of the reactor WWR-M was as follows: 24 hours at 10^{13} n·cm^{-2}·sec^{-1} [7] gave the sensitivity of about 10^{-8} g for ^{134}Cs and for ^{134m}Cs about 10^{-7} g. Because of the above and also taking into account the greater convenience of long-lived activity, we have chosen ^{134}Cs for cesium identification.

Due to large random variations of the sample shapes, the determination of the total cesium content in the samples by direct comparison with the standard activity would have led to considerable errors. Therefore, to measure the sample activity, water solutions obtained by cesium lixiviation from ceramics were used.

The removing of the surface layers from the samples was performed by fusing the ceramics with KOH and subsequently dissolving the melt in water.

A. Experiment

The ceramic samples were placed for irradiation in a quartz ampule with ground stoppers. Weighed amounts (2 mg) of CsCl served as the irradiated standards; they were welded in quartz ampules. In these experiments the cesium content in the sample in most cases was no less than 10^{-5} g; therefore, the activation was performed in an integral flux of 10^{16} n/cm^2. This corresponded to the minimal activity of 5 counts/sec for the line 605 keV. (We used the analyzer AY-100 with scintillator detector and NaI(Tl) crystal 40 mm × 40 mm in size). Figure 1 shows the typical gamma spectrum obtained without sample destruction. As the integral flow was small, the presence of the radioactive isotopes of the base material and of the impurities does not prevent the cesium detection. The cesium extraction from the whole samples as well as from the samples crushed to powder has been investigated. Figure 2 shows the influence of the ceramic powder boiling duration on the relative changes of the solution specific activity. The fourth point represents the result of secondary boiling in a fresh portion of water. To avert the radioactive

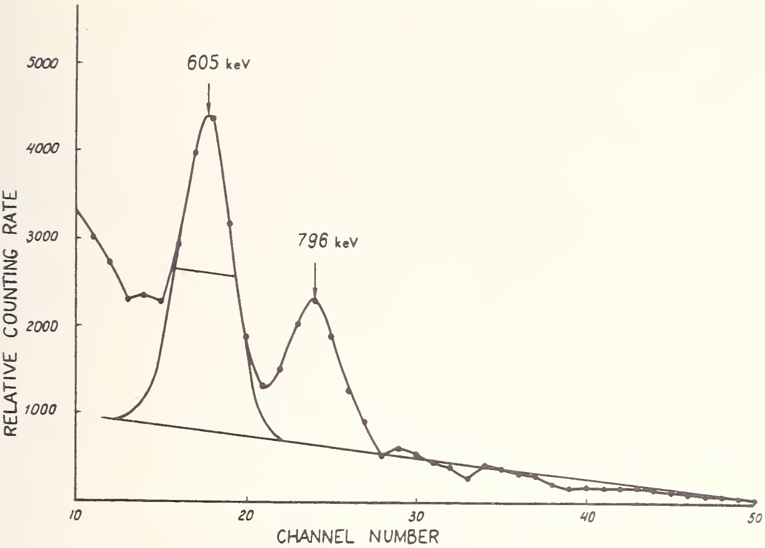

Figure 1. Gamma-spectrum of Al_2O_3 + 1% Y_2O_3 ceramics sample, that sorbed 10^{-5}g Cs after the activation with an integral flux of 10^{16} n/cm² after standing before measurement for 13 days.

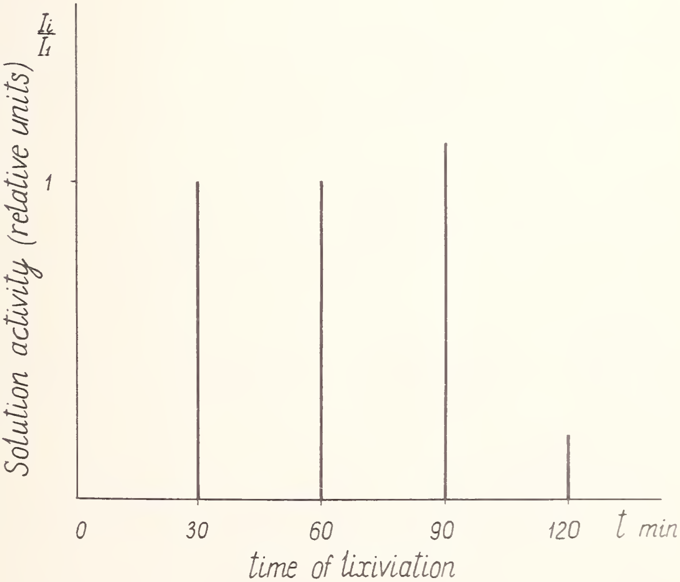

Figure 2. The effect of the lixiviation boiling duration on the relative variation of specific activity of the solution. Lixiviation during 120 min was made in the fresh portion of water.

cesium loss, a carrier (2×10^{-4} g/ml) was added to the solution. Figure 3 shows a diagram representing the extent of cesium extraction (residual activity) from sample pieces of ceramic. The straight line perpendicular to the abscissa corresponds to the initial sample activity taken for 100%. The extraction of four types of high clay ceramics has been investigated. The comparison of the activity obtained by 30 minutes boiling of the water solution with the activity of the irradiated standard gave the estimate of the total cesium content in the sample.

To determine the cesium penetration depth in the ceramic sample the fourfold chemical microtoming was carried out. The latter was made by fusing the sample with KOH in nickel crucible during 20 min at 500 °C and by subsequent dissolving of the cold melt in water.

The thickness of the removed layer was determined by weighing. The cesium amount in the removed layer was determined by the change of the sample activities before and after fusion.

B. The Results and Discussion

The ceramic samples obtained were numbered after cutting all three ceramic rings. The samples having numbers multiple of three were crushed to powder and were used only for determining the total cesium content.

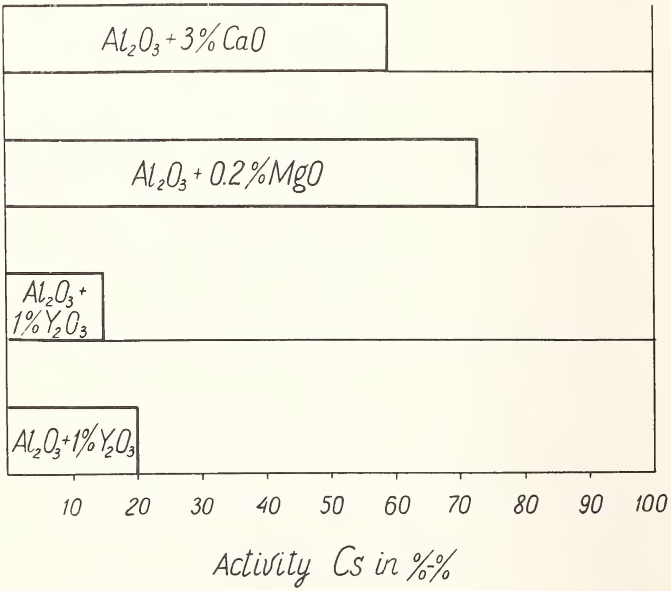

Figure 3. Residual activity after 30 min boiling for four types of ceramics. Initial activity was taken for 100%.

Table 1 shows the typical results of the total cesium content determination (ring N 2). It can be seen, first of all, that all compounds of cesium with ceramics are well dissolved in water, and secondly, the cesium lixiviation by water occurs irregularly over the sample proving the microinhomogeneity of the ceramics.

Table 2 presents the average results of the layer-by-layer determination of cesium concentration in the samples after water treatment.

The given average values of the removed ceramic layer thickness and of the corresponding cesium concentration show that the cesium absorption by the ceramics occurs mainly not by the diffusion probability

Table 1. Total contents of cesium in Al_2O_3 + 1% Y_2O_3 ceramics.

Sample No.	Weight in g	Part of Cs in H_2O %	Total contents Cs (g) × 10^4	Residual Cs after boiling (g) × 10^4
7	0.6433	58.2	1.0	0.42
8	0.6975	63.9	0.78	0.28
9	0.6120	100.0	0.60	–
10	0.6950	57.5	0.98	0.42
11	0.6672	58.0	1.16	0.44
12	0.6412	100.0	0.85	–

Table 2. Layer–by–layer average concentration of cesium in Al_2O_3 + 1% Y_2O_3 ceramics.

	First layer thickness (cm × 10^4)	Second layer thickness (cm × 10^4)	Third layer thickness (cm × 10^4)	Fourth layer thickness (cm × 10^4)
Ring No.	Concentration g/cm^3 (× 10^4)	Concentration g/cm^3 (× 10^4)	Concentration g/cm^3 (× 10^4)	Concentration g/cm^3 (× 10^4)
1	14.99 / 26	24.5 / 51	22.0 / 18	22.0 / 15
2	18.1 / 39	22.8 / 55	20.9 / 17.1	20.8 / 24
3	24.1 / 78	24.3 / 49	27.1 / 35	33.0 / 49

laws, but is accompanied by chemical reactions resulting in formation of the layer with approximately homogeneous distribution of the diffusing component [8].

Table 3 shows the cesium penetration depth estimates obtained from the average values of the concentration; besides this, the total cesium content per unit area of the sample surface is given, and the metallographic estimates of the cesium penetration in ceramics are also presented.

Table 3. Total contents per unit surface area and the penetration depth of cesium in the ceramics.

		Cs penetration depth cm × 10^4	
Ring No.	Total contents g/cm^2 per 1 cm^2	Activation analysis	Metallographic analysis
1	7×10^{-5}	60	80 – 100
2	8×10^{-5}	50	80 – 100
3	3×10^{-4}	150	180 – 200

The AA gives the integral estimate of the cesium penetration depth, and the zone width in which the grain distribution due to the cesium reaction is visible was determined metallographically. Therefore, the agreement of the results has to be considered as a good one. The agreement of the data for the rings N1 and N2 and some difference for the ring N3 seem to be connected with the average grain size, about 40 μm for the first two rings and about 100 μm for the third ring.

III. The Measurement of the Evaporation Rate of Molybdenum and Zirconium Carbide in Vacuum

There are three means of measuring the condensate activity: 1. direct gamma-spectroscopic analysis, 2. preliminary removal of the condensate from the collector and 3. preliminary isolation of the radioactive isotope from the removed condensate.

Our investigations have shown that the following scheme of condensate determination is optimal; the collector is subjected to the neutron irradiation; the collector surface layer is etched chemically (together with the condensate), and then the activity of the solution obtained is measured. If necessary some radioactive isotopes can be selected from the solution. Since good cooling of collector is necessary, it has to be made of metal which besides good thermoconductivity must fulfill two more conditions: it must withstand the irradiation in powerful neutron and gamma fields of the reactor, and it must have small self-activity at the end of the irradiation or after a short "cooling down" time. Three metals satisfy these requirements: lead, aluminum and titanium. Lead was selected as a collector material.

A. EXPERIMENT

The evaporation was made in a metal apparatus with rubber gaskets; operating pressure was 10^{-5} to 10^{-6} mm Hg. Figure 4 shows the scheme of the apparatus. The rods 40 mm long and 1.7 to 2 mm diameter were fixed on the massive water cooled leads by tantalum collars, the ends of the rods being in contact only with tungsten sheets placed under the tantalum collars (Fig. 4B). The rod was surrounded by a screen with

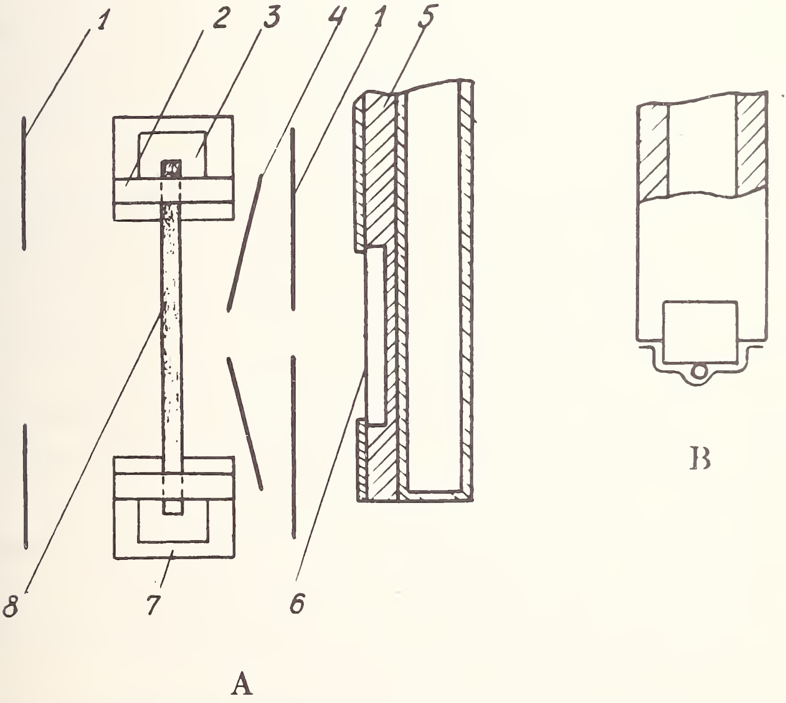

Figure 4. A. The schematic of the evaporation apparatus; 1—Tantalum screen; 2—Tantalum collar; 3—Tungsten support; 4—additional tungsten screen; 5—Water-cooled copper collector disk; 6—Lead collector; 7—Heating current water-cooled leads; 8—Zirconium rod; B. Schematic of ZrC rod fixing to the current lead.

two windows. Another one limits the flux of evaporated substance from only the central part of the rod with temperature difference of not more than 20 to 40 °C. Lead plates about 2 mm thick were pressed to the copper water cooled disk and were used as the collectors. Four collector plates were placed simultaneously. The lead plates with the evaporated substance deposited were subjected to the neutron irradiation, and then the AA was carried out. The evaporation rate was calculated from the formula:

$$v = Ab \frac{\Delta p}{\Delta t}$$

where Δp is the condensate weight in grams, and Δt is the evaporation time in seconds.

Factor $b = 1.13$ takes into account the percentage of zirconium in ZrC if we believe ZrC to evaporate congruently ($b = 1$ for Mo). Factor A takes into consideration first of all the part of the flux of evaporating substance which gets on the collector which is determined by the solid angle under which the collector is seen through the window in the screen; and secondly the directional distribution law of the evaporated particles (cosine law). Factor A is determined by the calculation and is checked experimentally by the known evaporation rate of tantalum. For molybdenum rods 2 mm diameter, $A = 20.4$, and for ZrC rods 1.75 mm diameter, $A = 23.2$.

The condensate was removed by dissolving the collector surface in the cold acid mixture (two parts of HNO_3 (1:1) and one part of concentrated HF) for 1 min. Then 0.5 ml of the concentrated sulphuric acid was added to the solution and this solution was evaporated. In case of ZrC the carrier was added before evaporation. The relative error of the reproducibility of single etching of lead was 12% (confidence probability 0.9), with the average amount of the dissolved lead being 0.05%.

The completeness of the condensate removal was checked by more strongly absorbed molybdenum. In this case a single etching transfers more than 90% of the condensate into solution.

Activation conditions are as follows: 2 hours at 10^{13} $n \cdot cm^2 \cdot sec^{-1}$ identification by ^{99}Tc (gamma line 140 keV, allowed to stand before measurement for about 30 hours to establish the equilibrium of the reaction $^{99}Mo \rightarrow {}^{99}Tc$). The results are shown in Figure 4. The other data [9] are given for comparison. The squared error of the average value is calculated for the confidence probability 0.9.

Since the evaporation rate of ZrC is about two orders of magnitude less than that of molybdenum with the same conditions, the integral neutron flux was used at about two orders larger than in the case of ZrC. In the latter case, the impurities in the collector material and in the ZrC, mask the Zr gamma line. According to the data of the activation determination,

Table 4. The evaporation rate of molybdenum vs temperature.

	Evaporation rate $g \cdot cm^{-2} \cdot sec^{-1}$	
Temperature °C	Present work	Data [9]
1940	$(5.4 \pm 1.1) \times 10^{-8}$	1.36×10^{-7}
2140	$(5.7 \pm 1.4) \times 10^{-7}$	2.32×10^{-6}

the main impurities of the condensate solution are: Sb$\sim 10^{-6}$g, Zn$\sim 3 \times 10^{-6}$g, Ta$\sim 4 \times 10^{-8}$g and Hf$\sim$ 10^{-7}g. All of them have activation cross sections much larger than that of zirconium. Chemical selection of ^{95}Zr was performed according to the scheme shown in Figure 5. The carrier solution (a water of solution of $ZrOCl_2$) contained 4.5×10^{-3}g/ml of zirconium. The principal hindering activities in the condensate solution were ^{182}Ta and ^{65}Zn. The latter was separated without the carrier together with the AgCl precipitate. The hold-back carrier was added for the removal of tantalum and the separation was carried out by the fluorine-tannin method [10]. The hold-back carrier solution contained 10^{-3}g/ml of tantalum and was prepared by dissolving Ta_2O_5 in HF with further evaporation to a drop and dissolving in HCL (1:1). The similar cycle of Zr isolation was performed for the irradiated standards. (10^{-3}g Zr in $ZrOCl_2$ weighted amount). Average chemical yield of the cycle was 90%.

The measurement of the ZrC evaporation rate was made at four temperatures: 2050 °C, 2160 °C, 2275 °C and 2380 °C. The plot of log ν vs $1/T$ (Fig. 6) is a straight line nearly parallel to the same plot for the ZrC powder (about + 50% porosity) deposited on the tungsten ribbon [3-5]. The rods in these experiments had 7 to 15% porosity. The data of other authors [11] for higher temperatures are shown in the same figure.

Some discrepancy observed for different results can be connected with the different methods applied and with variations of properties of ZrC of different origin.

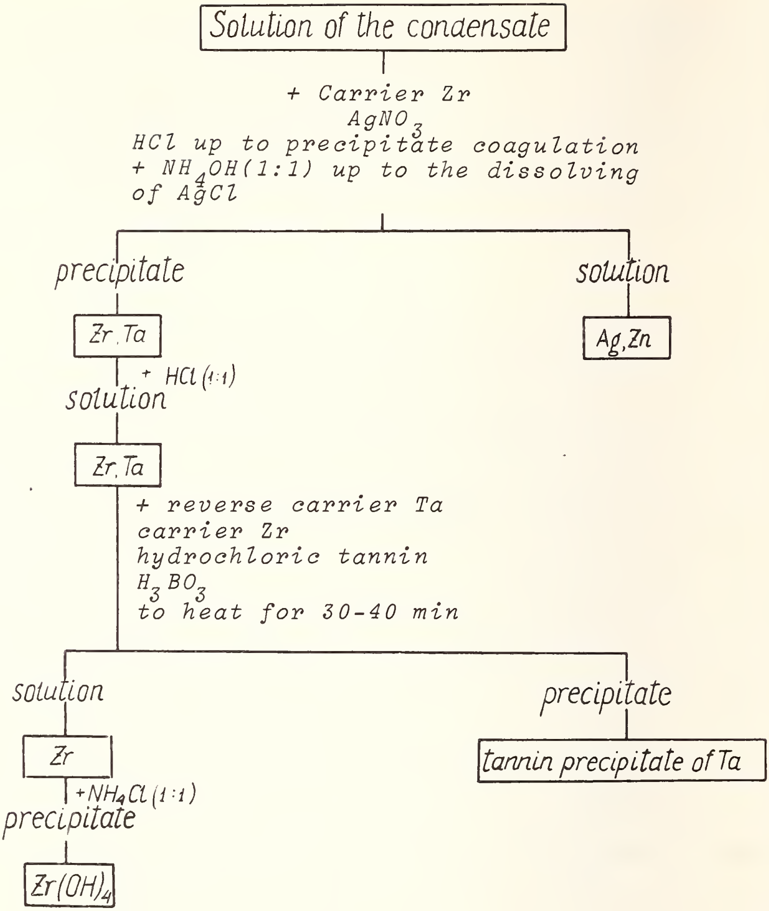

Figure 5. Schematic of ^{95}Zr chemical isolation procedure from irradiated ZrC condensate solution obtained after etching.

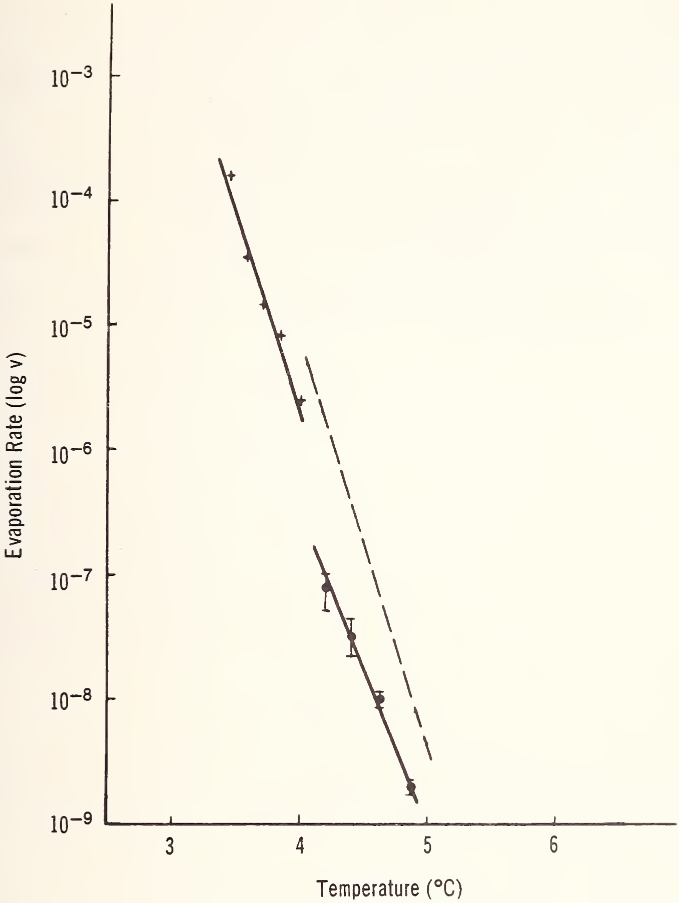

Figure 6. Plot of ZrC evaporation rate vs temperature: ...new data; ---data for ZrC powder [5]; +++data from [8].

IV. References

[1] Ryskin, G. Ya, Fiz. Tverd. Tela **1,** No. 6, 952 (1950).

[2] Ascoli, A., and Germagnoli, E., Proc. of the Radioactivation Analysis Symposium, Vienna, June 1959. Pure and Appl. Chem. **1,** 139-141 (1961).

[3] Maslov, I. A., and Obukhov, A. P., Transactions of the First All-Union Conference on Activation Analysis, Tashkent Branch of the Academy of Sciences, 33-79 (1964).

[4] Maslov, I., Wiss. Zeitschr. Techn. Hochsch. Chemic **6,** No. 2, 113 (1964).
[5] Karnaukhova, N. M.,Zh. Tekh. Fiz. **6,** No. 2, 113 (1964).
[6] Schmied, H., and Deak, M., Brit. J. Appl. Phys. **16,** No. 2, 269 (1965).
[7] Maslov, I. A., Collection "Methods for Analysis of Substances of High Purity", "Nauka" Publishing House, 91 (1965).
[8] Barrer, R. M., Diffusion Through Solids, Cambridge University Press, Princeton, 1951.
[9] Golubtsov, I. V., and Nesmeyanov, A. N., Vestnik MGM (Herald of the Moscow State University), Series 11, Chemistry **5,** 31 (1965).
[10] Marochevskiy, Yu. V., and Knipovich, Yu. N., editors, "Analysis of Mineral Raw Materials", State Chemical Publishing House, 670 (1959).
[11] Fesenko, V. V., and Bolgar, A. Ye, "Vaporization of Refractory Compounds", Metallurgiyo 86 (1966).

DIVERSIFIED INSTRUMENTAL NUCLEAR ANALYSIS METHODS USING A REACTOR

H. W. Nass

Union Carbide Corporation
Sterling Forest Research Center
Tuxedo, New York 10987

I. Introduction

The most satisfying nuclear analyses are those that are rapid and nondestructive. The intent of this paper is to briefly summarize several of the unique instrumental nuclear analysis methods that are readily adaptable to a reactor facility but are often overlooked. These methods include the use of cadmium-covered irradiations to suppress the production of interfering radionuclides, the determination of deuterium by the photoneutron method, the determination of the uranium by the delayed neutron method, and the use of solid state detectors to resolve short-lived radionuclides of interest in the presence of other radionuclides of similar gamma-ray emissions.

II. Experimental

In all but the photoneutron method, sample irradiations were made using one of the pneumatic shuttle tubes terminating at the face of Union Carbide Corporation's 5-MW swimming pool reactor with thermal neutron fluxes ranging from 2-3 × 10^{13} $n \cdot cm^{-2} \cdot sec^{-1}$. The detection equipment utilized either one of several 400 channel multichannel analyzers attached to 3 in. × 3 in. NaI(Tl) detectors; a 1600 channel multiparameter analyzer attached to a 36 cm^3 Ge(Li) detector; or standard transistorized scalers attached to neutron detectors such as the BF_3 or ^3He. Figure 1 shows the pneumatic tube system with the recording clocks [1], while Figure 2 shows a flow diagram of the data arising from the irradiated samples to the printed out results from the computer.

A. CADMIUM-COVERED IRRADIATIONS

The analytical indicators used in thermal neutron activation analysis are produced by both thermal neutrons and neutrons of a higher energy such as epicadmium neutrons. The percentage of the analytical indicator that is produced by thermal neutrons and that produced by epicadmium

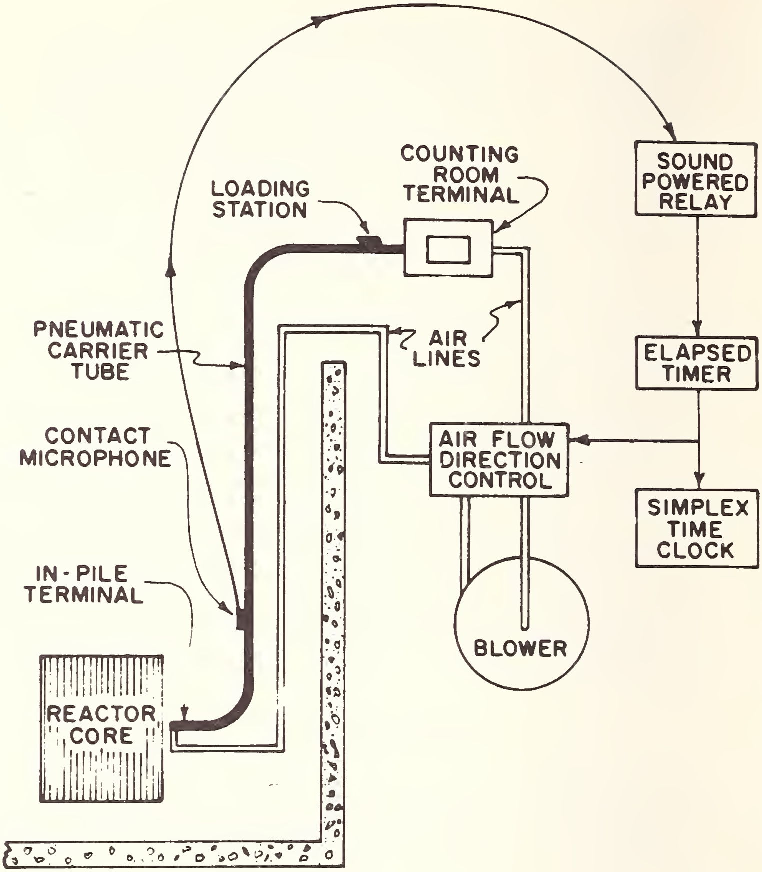

Figure 1. Pneumatic tube and control system.

neutrons varies from nuclide to nuclide, and this variation can be quite large. In our reactor, it can range from a cadmium ratio of less than three to a cadmium ratio of greater than 100 (Table 1). By simply irradiating a sample in a cadmium cover, one can reduce interfering radionuclides which are of a high cadmium ratio permitting the direct detection of the radionuclides of a low cadmium ratio. A typical example is the determination of bromine in seawater or human blood (Figs. 3 and 4).

The analysis for bromine in various materials is accomplished by packaging samples and standards in slim polyethlene vials which fit inside the cadmium liners, Figure 5. The samples and standards are then irradiated for 1.0 minute. After irradiation, containers are removed from the cadmium-lined rabbits and washed in HNO_3-H_2O-Acetone solution to remove surface activity and allowed to dry. After a decay of ~15-20

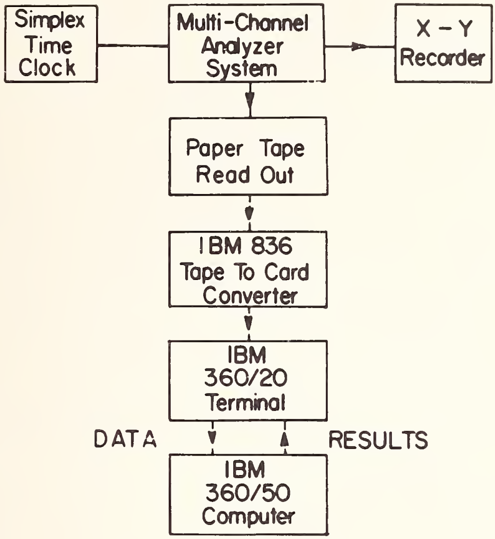

Figure 2. Flow of analyzer data.

Table 1. Cadmium ratios in Union Carbide reactor.

Isotope	Cadmium ratio for production
^{80}Br	4.0
^{128}I	3.0
^{105}Ru	3.9
^{179m}Hf	2.6
^{110}Ag	4.8
^{187}W	5.9
^{198}Au	2.5
^{24}Na	67.
^{56}Mn	37.
^{38}Cl	65.

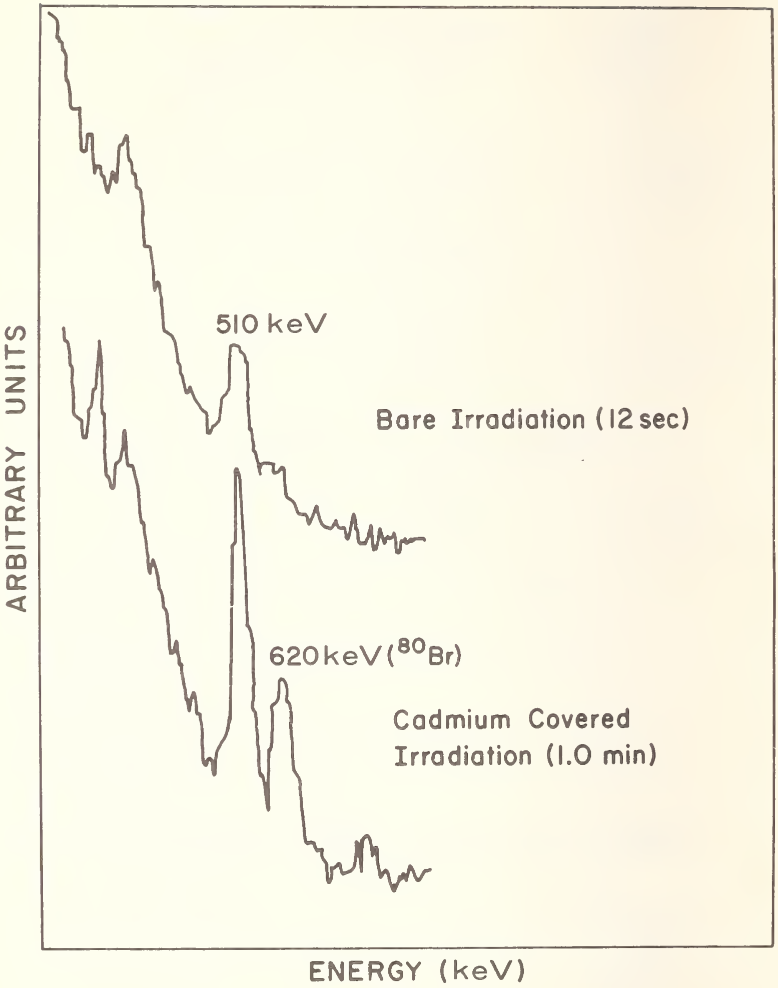

Figure 3. Bromine in whole blood.

minutes the samples are counted for 10 minutes on either the Ge(Li) system or a NaI(Tl) system, depending on the activity and interferences. Table 2 shows results of several analyses.

B. DEUTERIUM ANALYSIS

In the photoneutron method for the analysis of deuterium, samples are subjected to high energy gamma rays which liberate a neutron from the deuterium nucleus by the $^2H(\gamma,n)^1H$ reaction. The liberated neutrons are then counted using a neutron detector-scaler system (Fig. 6), allowing

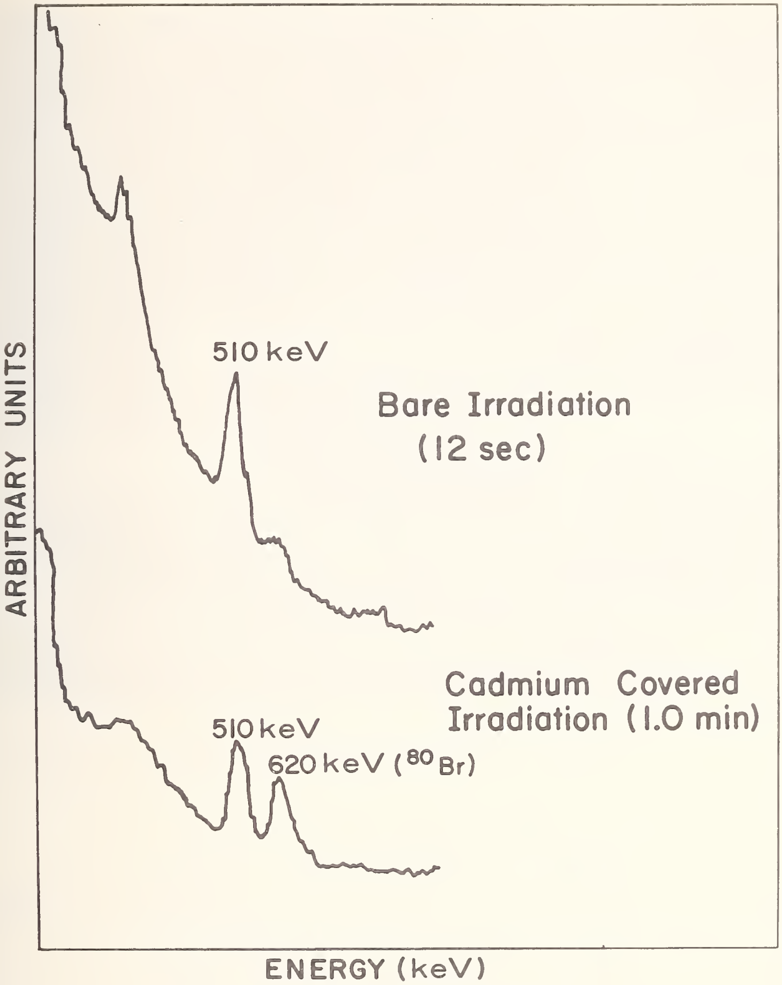

Figure 4. Bromine in seawater.

quantitative measurement of deuterium down to 2 micrograms. The photoneutron method is not widely used because of the small samples normally available for such tests, because of radiation hazards associated with the strong gamma-ray sources needed to give usable detection sensitivities, and because of the relatively short half life of the most convenient radioisotope source (^{24}Na; $T_{1/2} = 15$ hrs.). These last two limitations, however, pose no problems at reactors where hot cell facilities are available for shielding and the reactor is used to activate multicurie ^{24}Na sources. A demonstration of the use of the photoneutron method was the analysis of deuterium in a number of body-water samples

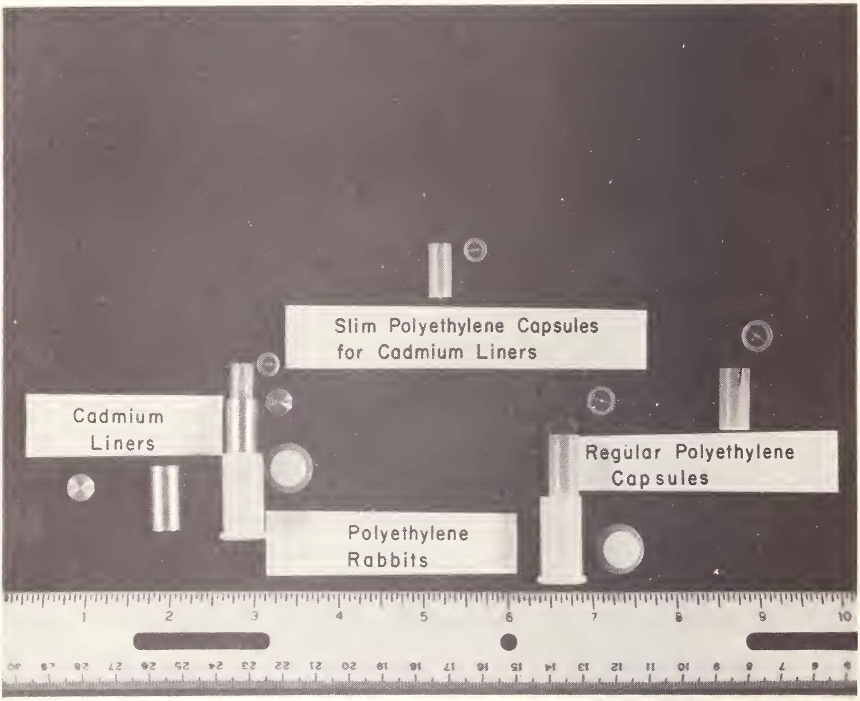
Slim Polyethylene Capsules for Cadmium Liners
Cadmium Liners
Regular Polyethylene Capsules
Polyethylene Rabbits
1
2
3
4
5
6
7
8
9
10

Figure 5. Rabbits, capsules and cadmium liners.

Table 2. Results of bromine analyses.

Sample	Type[a]	NaI(Tl)	Ge(Li)
Serum	CC	9.0	12.
	B	<80.	<30.
Whole Dry Blood	CC	16.	13.
Beef Liver	CC	4.2	5.7
	B	<1800.	<200.
Beef Muscle	CC	16.	17.
	B	<20.	<18.
Fish Meal	CC	20.	19.
	B	<60.	<20.

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[a] CC = Cadmium–covered irradiation 1.0 min.
B = Bare irradiation 0.2 min.

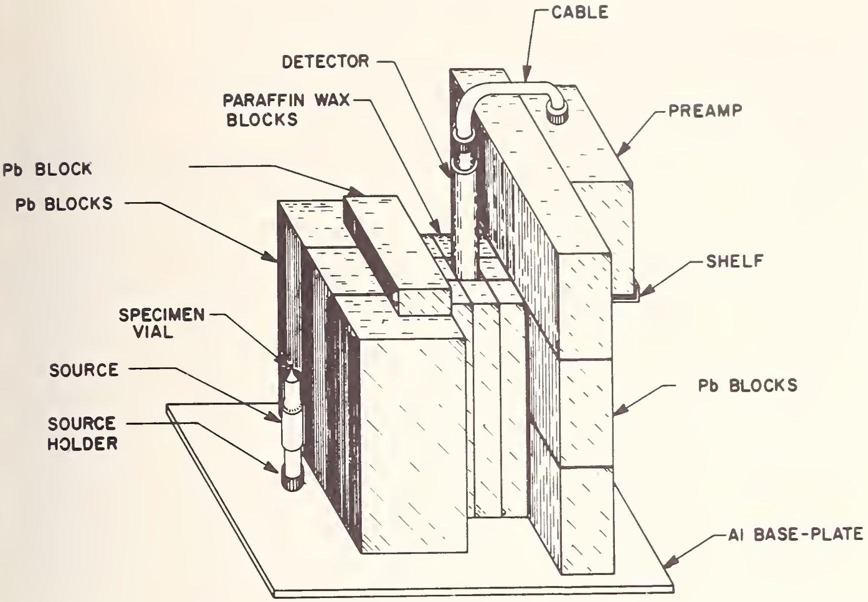

Figure 6. Photoneutron system (Deuterium analyzer).

previously analyzed by several other techniques (Table 3). The results obtained by the photoneutron method were in excellent agreement with those obtained by the other techniques [2].

C. Uranium Analysis

Analysis for ^{235}U or total uranium can be most easily completed by counting the neutrons emitted in the decay of a number of short-lived fission products from the fission of uranium-235. If natural abundance in the sample of uranium can be assured, the total uranium content of the sample can be determined. These analyses can be completed in less than two minutes each with sensitivities down to 0.05 micrograms of uranium. As in the photoneutron method for deuterium, this technique is virtually matrix independent and permits direct analysis for uranium in a wide variety of matrices (Table 4). The equipment necessary for this type of analysis is a pneumatic tube system, and a very simple neutron detector-scaler system (Figs. 7 and 8). The system used in our laboratory is very similar to that developed by the Oak Ridge National Laboratories [3].

D. The Ge(Li) *vs.* The Na(Tl) Detectors

The primary advantage of the Ge(Li) detector over all others is a 10-50-fold increase in resolution for gamma rays; hence, a marked

Table 3. Results of deuterium analyses.

	Deuterium concentration, volume percent				
Sample identification	Photoneutron method	Gas[a] chromatography	Falling[a] drop	Osmometry[a]	Infrared[a]
0 × 12	0.308, 0.312	–	0.31	0.31	–
0 × 15	0.272	–	0.27	0.27	–
0 × 17	0.323	–	0.32	0.17	–
R × 1	0.245, 0.230	0.24	0.31	0.29	0.23
25N	0.130, 0.142	0.24	0.26	0.28	0.16
26N	0.245, 0.234	0.31	0.31	0.30	0.25
29N	0.145	0.14	0.19	0.17	0.13
31N	0.187	0.25	0.28	0.22	0.20
B–13	0.226, 0.226	–	0.27	0.21	0.23
O–29	0.168	–	0.18	0.18	0.15
O–30	0.283	–	0.29	0.29	0.24
O–351	0.336	–	0.32	0.33	0.27
31R	0.276, 0.268	0.24	0.28	0.32	0.24

[a] Values accompanying samples.

simplification is achieved in the analysis of samples which produce a complex gamma-ray spectra. However, associated with the increase in resolution is normally a hundred-fold decrease in sensitivity. Thus, it would appear that the most sensitive detector system would be that of the Na(Tl) type. However, this is not always the case in purely nondestructive methods as is shown with the analysis of selenium when using ^{77m}Se as the analytical indicator. Selenium-77m is the most sensitive analytical indicator for selenium when using the thermal neutron activation technique. However, the analyst must be prepared for interferences by ^{46m}Sc and ^{19}O (Figure 9) when using the NaI(Tl) detectors. These interfering radionuclides are, however, resolved as discrete gamma-ray emissions when using the Ge(Li) detector (Figure 9).

Although the integrated photopeaks are normally larger using the sodium iodide detectors, the interferences from both scandium and oxygen tends to mask ^{77m}Se in most samples. The Ge(Li) system, although having smaller total photopeak areas, has sufficient resolution so adjacent gamma rays do not interfere and a reasonably high peak-to-photopeak area ratio so that peaks are observable down to concentration levels (Table 5) lower than that obtainable with the same sample using a NaI(Tl) detector. Hence, when picking a detector to do the analysis, one must not only consider the intrinsic resolution and efficiency, but one

Table 4. Results of uranium analyses.

Sample	Analyzed for	Delayed neutron results[a]	Other methods Type	Other methods Results
U–Ore	Total U (Natural)	0.16%	Chemical	0.14%
			NAA[b]	0.13%
			Radiometric	0.16%
Th–Ore	Total Th	1.00%[c]	Chemical	1.01%
	Total U (Natural)	410 ppm	Chemical	400 ppm
Dirt–1	Total U	6.0 ppm	NAA	6.2 ppm
Dirt–3	(Natural)	1700. ppm	NAA	1900. ppm
Plant–2	Total U	396. ppm	NAA	350. ppm
Plant–3	(Natural)	2.8 ppm	NAA	2.6 ppm
Water–2	Total U (Natural)	1.2 ppm	NAA	1.0 ppm
Water–3	^{235}U (Enriched)	7.1×10^{-7} g	Chemical	7.3×10^{-7} g
Stream Sediments–1	Total U	521. ppm	NAA	558. ppm
–2	(Natural)	4.4 ppm	NAA	4.2 ppm

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[a] The results have an estimated relative standard deviation of 10%.

[b] By the ^{238}U(n, γ) ^{239}U method.

[c] Measured with bare and cadmium–covered irradiations.

must also consider the extent to which other interferences do affect the analysis.

III. Summary

Four techniques have been described that are seldom used but can be used to a great advantage and can often be implemented at most reactor facilities with minimal effort and costs. The examples chosen to illustrate these methods are not the only application of these methods. For example: we routinely use cadmium covers in the direct instrumental analysis of Ag, Ru, Au, W and I; Be can be analyzed by the "deuterium" photoneutron apparatus down to 50 μg, the delayed neutron counting chamber can be used to analyze Th with about 1/100th of the sensitivity

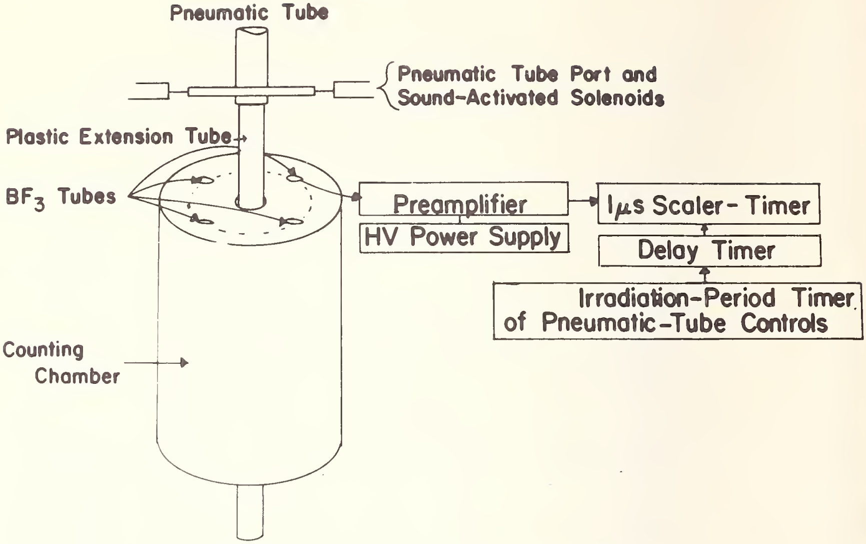


Figure 7. Delayed neutron system outline.

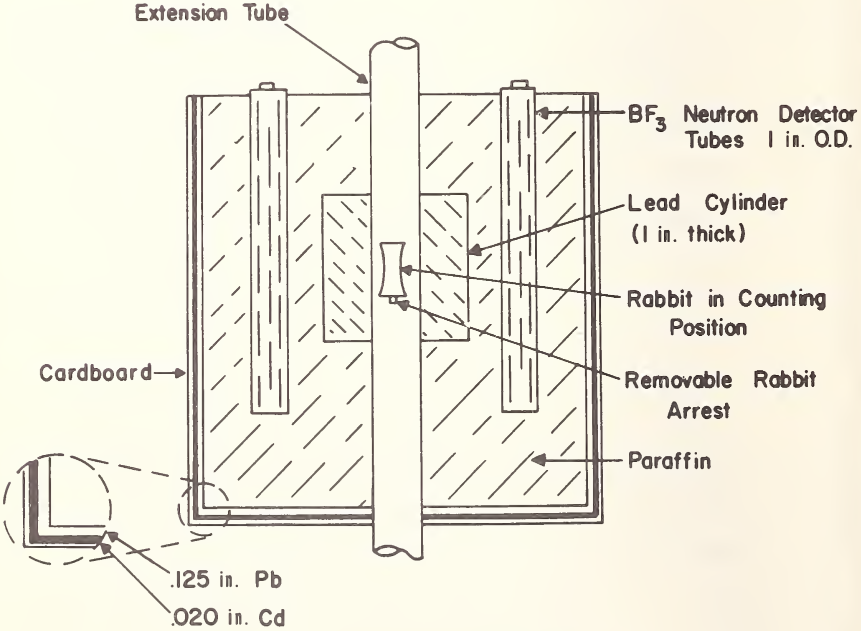


Figure 8. Delayed neutron counting chamber.

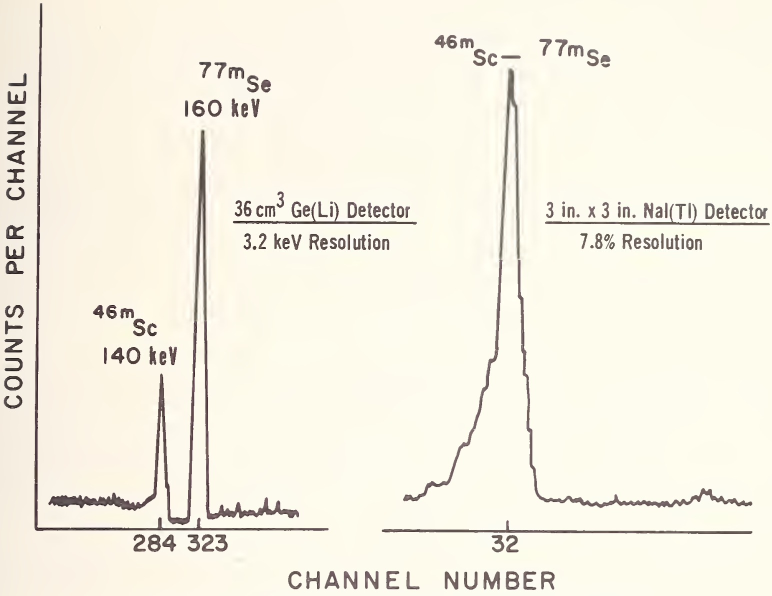


Figure 9. Gamma-ray spectrum of selenium in alfalfa.

Table 5. Results of selenium analyses.

Sample	Selenium (Ge(Li)	 NaI(Tl)
Fish Meal	1.2	1.1
Whole Dry Blood	0.39	<0.4
Hair	0.78	<4.
Beef Liver Dry	0.39	<0.4
Blood Serum	0.095	<0.7
Clover	<0.06	<0.4

for U, and the techniques applied for Se can just as easily be used in the analysis for the short lived indicators of Ag, Sc, Rh and F. In each case, the analyses are nondestructive, rapid, simple and undoubtedly would provide a valuable tool at virtually any reactor site.

IV. References

[1] Nostrand, J. W., Jr., and Kramer, H. H., "Computer Integrated Activation Analysis", Reprint 2.4-2-64. Instrument Society of America 19th Annual ISA Conference.

[2] Graystone, J., et al, "Measurement of D_2O in Plasma Water by Freezing Point Elevation, Falling Drop, Infrared Absorption and Gas Chromatography", J. Lab. and Clin. Med., May 1967.

[3] Dyer, F. F., Emery, J. F., and Leddicotte, G. W., ORNL 3342 (October 1962).

MAJOR CONSTITUENTS DETERMINATION IN SUBSTANCES BY ACTIVATION ANALYSIS

Carmelo Cappadona

Istituto di Applicazioni e Impianti Nucleari
Facolta' di Ingegneria
University of Palermo
Palermo, Italy

I. Introduction

Until now activation analysis has been employed as a sensitive tool for the determination of traces and minor constituents, but this method has not been considered available for macroconstituents, at least in the cases which require radiochemical separations with an isotopic carrier after irradiation.

This technique really is not executable because the concentration of the macrocomponent compared with the weight of the carrier is not negligible.

Nevertheless, having resorted to a technique of activation [1] and isotopic dilution [2,3], we have carried out a simple general method for macrocomponent determination of a substance which is more suitable in many cases than the chemical analysis, specially with some complex materials or in routine determinations.

II. Experimental

A sample of the substance chosen for the analysis is irradiated and dissolved with a suitable reagent. The necessity of the standard is avoided. An aliquot is taken from the solution and the qualitative separation of the macroelement desired is carried out. The specific activity, α_1, of the macroconstituent is now evaluated by measuring the activity and weight of the separated sample. A known amount of isotopic carrier is added to the remaining solution and the macroconstituent is separated as before. Finally, the specific activity, α_2, of this specimen so treated is measured.

We call now:

x = macrocomponent chosen for the analysis,
P = weight unknown of x,
V = volume of the whole solution,
V_1, V_2 = volumes of the 1st and 2nd aliquot,

$A_1, A_2; P_1, P_2$ = weights and activities of the macroconstituent, x, separated from the 1st and 2nd aliquot,
C = weight of the carrier added in the 2nd aliquot,
a, p = activity and weight of x referred to the unit of volume of the solution V.

Now we have the relations as follows: $P=pV$; $P_1=pV_1$; $P_2=pV_2$; $A_1=aV_1$; $a_2=aV_2$; and

$$\alpha_1=\frac{A_1}{P_1}=\frac{aV_1}{pV_1}=\frac{a}{p} \tag{1}$$

$$\alpha_2=\frac{A_2}{P_2+C}=\frac{aV_2}{pV_2+C} \tag{2}$$

From the (1) and (2) is obtained:

$$\frac{\alpha_1}{\alpha_2}=\frac{pV_2+C}{pV_2}$$

$$pV_2=\frac{\alpha_2}{\alpha_1-\alpha_2}C$$

$$P=\frac{\alpha_2}{\alpha_1-\alpha_2}C\frac{V}{V_2} \tag{3}$$

An example of this method is done by the determination of the gold in Au-Cu alloys, as follows: A sample of about 100 mg is irradiated and dissolved with aqua regia diluting the solution to at least 50 cm³ with distilled water. An aliquot of 40 cm³ is taken and the remaining 10 cm³ are treated with gold chloride containing 50 mg gold carrier. The two aliquots are heated and treated successively with H_2O_2 in order to precipitate the gold as sponge or as metallic scales. The precipitates are purified with HCl, washed, dried, and weighed. Their activities are finally measured for the evaluation of the specific activities.

This following relation is used to estimate the weight of gold:

$$P=\frac{\alpha_2}{\alpha_1-\alpha_2}50\frac{50}{10}\text{ mg} \tag{4}$$

III. Results and Discussion

The method has been applied by us [4] for the quantitative analysis of some macroconstituents of alloys such as Au, Sn, P, Cu; and the error has been less than 1%. The best precision has been attained by means of the calculations of the average of some counting measurements.

Moreover, this technique avoids the necessity of a standard, leaves out the errors due to self-shielding, enhancement, resonance, and variations of the neutron flux or charged particles, and in some cases avoids the errors derived from eventual secondary reactions as, in the instance of the gold determination, the production of ^{199}Au.

The method appears to be a useful tool for the analysis of major constituents in some complex materials and can be performed in more cases after carrying out the activation analysis of the minor constituents in a sample.

IV. References

[1] Cappadona, C., Proc. 1965 Intern. Conf. Mod. Trends in Activation Analysis, College Station, Texas, p. 363.

[2] Hevesy, G., and Hobbie, R., Z. Analyt. Chem. **1**, 88 (1932).

[3] Wahl, A. C., *et al,* Radioactivity Applied to Chemistry, John Wiley, New York, 1958, p. 94.

[4] Cappadona, C., *et al,* Work in process of publication.

RADIOCHEMICAL SEPARATIONS FOR ACTIVATION ANALYSIS

Plenary Lecture by F. GIRARDI

Chemistry Department
European Community Joint Nuclear Research Center
Ispra Establishment
Ispra, Italy

I. Introduction

Radiochemical separations have always been an essential part of many activation analysis applications. The continuous development of detectors and instrumental procedures which increase the possibilities of nondestructive analysis has not eliminated the need for radiochemical separation, but certainly has put less stringent requirements upon these separations. Often a general group separation or the elimination of a few interfering radionuclides can now be considered a satisfactory solution to problems which require the destructive sample approach.

The development of selective instrumental procedures will certainly continue, but this does not necessarily imply that the need for radiochemical separations will correspondingly diminish. The demand for quantitative analysis has in fact undoubtedly changed during recent years both in amount and nature. There are many reasons for these changes which are found more or less in all the areas of application. One reason is the spectacular growth of other analytical techniques which can solve many quantitative analyses in the parts per million range in an efficient and economical manner. Among these, atomic absorption spectroscopy has lead to instruments which can be operated very simply by nonspecialized personnel and which give sensitivities often approaching those of activation analysis provided a large sample is available. The cost of these instruments is within reach of most analytical laboratories, and the cost of each individual analysis is very reasonable.

Another impact on the analytical field is a considerable augmentation of the requests for analysis partly due to the increased impact of science and technology, partly to the acknowledgment that trace elements are important, and that our knowledge about them is very little and uncertain.

A third phenomenon which is perhaps a consequence of the first two is an extention of the demand towards the parts per billion (ppb) range, and towards the analysis of unusual elements, which had previously been considered less important.

How these phenomena, the list of which could perhaps continue, will influence the applications and developments of activation analysis, could be a matter for discussion, but I would not be surprised if one of the dominant tasks for activation analysis in the future become analyses at the parts per billion level, most frequently on the less common elements.

For these applications activation analysis still has a great potential, perhaps much greater than any other analytical technique. The sensitivity which can be obtained with the neutron fluxes now available is indeed in the ppb range, or even lower. The limitation to full exploitation of this sensitivity is that major components will activate to such an extent that a chemical separation on a highly active sample becomes necessary.

Good radiochemical procedures are of course essential to reach this goal, and it could even be necessary to return to procedures yielding a very good radiochemical purity in order to take advantage of the high efficiency of beta-counters.

This does not mean that nondestructive analysis might loose importance in the future. There is, in fact, another area in which activation analysis has a great potential where most other techniques fail. This is activation microanalysis or analysis of extremely small samples. Here the nondestructive approach will clearly be the most elegant, although in some cases, chemistry might be required.

Radiochemistry must clearly adapt both to variations in demand and to the development of its partners, the activation sources and the radiation detectors. This is not a simple task since no easy mechanism presently exist for such an adaptation which is largely committed to the "chemical feeling" of the radiochemist.

Some work is however being done to simplify that task, and we shall come back on this point after a rapid survey of what is available nowadays to the radiochemist for his destructive analysis.

II. Sample Pretreatment

A. Definition

We define as "sample pretreatment" that preliminary step of each chemical separation by which the elements to be determined are transferred from the sample to a mineral solution for the successive application of standard methods of chemical separation. Partial separation may or may not be achieved during this preliminary step.

Pretreatment can be the most difficult step of the whole destructive analysis. The essential requirement is of course a quantitative transfer of the desired elements, and in many cases the completeness of transfer can indeed be difficult to prove. The elements in the pretreated sample should also be in one chemical form and stable with time.

B. Carrier Addition and Measurement of Chemical Yield

Carriers in μg to mg quantities are frequently added during pretreatment to simplify the successive steps of the separation and to allow measurement of its chemical yield.

In recent years the applications of chromatographic techniques which can be carried out quantitatively without the addition of carriers have introduced the possibility of avoiding both the addition of carriers and the determination of the chemical yields. Furthermore, while these techniques are simple and rapid on small amounts of material, they can become difficult and tedious with presence of milligram quantities of the carriers. Of course, the assumption that the separation is carried out quantitatively must be proved with exhaustive preliminary assays.

When a quantitative recovery is doubtful, and one still wants to retain the advantages of working with micrograms, the radioisotope dilution method of chemical yield measurement seems particularly useful and consistent with the existing developmental trends. It consists in adding a radiotracer, whose radioactivity can be distinguished from that of the activated product, and counting both radioactivities possibly simultaneously. This method seems particularly advantageous now when on the one hand the number of radioisotopes which can be distinguished by those produced by (n,γ) reaction is increased considerably through the commercial availability of many cyclotron produced isotopes, and on the other hand the use of high resolution Ge(Li) detectors and electronic computers enable a large quantity of data to be recorded from one counting operation. Thus, the measurement of the chemical yield can be included without any practical increase in operating time and cost.

Another very sensitive method of yield determination is of course activation analysis, and methods involving reirradiation of the counting sources have been used frequently. Improved accuracy and simplified procedures was obtained by also adding carriers of suspected interfering elements [1,2].

A way of avoiding the measurement of chemical yields, still conserving a high accuracy is the application of the substoichiometric principle [3].

When destructive analyses are carried out by this method, an equal amount of carrier of the element to be determined is added to both unknown sample and comparator. Chemical separations are then carried out in exactly the same way on both by various techniques with the care of employing a substoichiometric quantity of reagent. By this means the same quantity of the element is separated from both comparator and sample, and the ratio of the measured radioactivities is equal to the ratio of weights, as if a quantitative transfer was obtained.

Various techniques can be employed with the substoichiometric principle (precipitation, ion exchange, solvent extraction, electrodeposition . . .) but the widest applicability is certainly in solvent extraction systems [4-6]. Separations carried out with the substoichiometric principle can also be elegantly automated [7].

C. Techniques of Sample Pretreatment

Techniques for the pretreatment of samples are many, and comprehensive analytical textbooks deal extensively with the various possibilities in connection with the different analytical techniques used for quantitative analysis [8]. Techniques for dissolving samples after radioactivation are similar to these except that four characteristics of the activated samples offer for activation analysis advantages over conventional methods of analysis that are perhaps not fully exploited: (1) samples are usually small, and destruction requires less time and reagents, (2) carriers can be added, adsorption losses can therefore be much less than with conventional techniques, (3) sample pollution from partial attack of the reaction vessel is unimportant, and (4) gross measurements of radioactivity can permit a rapid check for absence of losses. They are widely different for inorganic or organic materials. The former require only a dissolution step, the latter require the mineralization of the organic matrix to which trace elements are generally bound.

1. Inorganic Matrices

a. Acid Dissolution. This is the simplest method particularly for many metallic samples. Anodic dissolution is a modification of the acid dissolution procedure which is satisfactory for many difficult materials such as graphite [9]. Techniques of acid dissolution (and wet ashing for organic materials) are perhaps the most convenient and reliable for sample pretreatment of radioactive materials. When the dissolution is done in a silica vessel connected to a reflux condenser there is a high probability that all the requirements of sample pretreatment have been met. The direct coupling to a distillation procedure also gives an initial separation into two groups with only limited additional effort. Although the time required may be long, many samples can be processed in parallel.

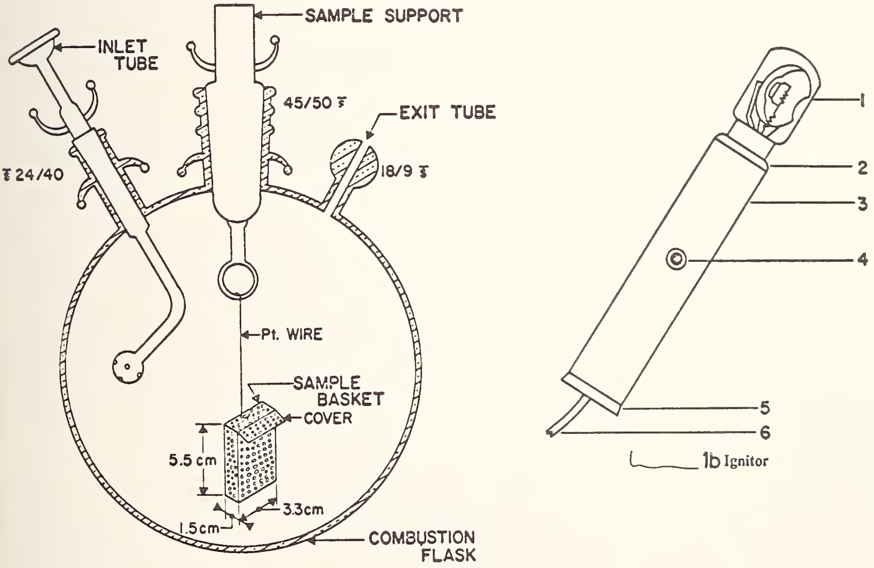
b. Fusion Procedures. These are frequently used for refractory oxides, rocks, ores *etc.,* which often cannot be treated satisfactorily by wet procedures. A large variety of melting mixtures are available for the various kind of samples [8].

Fusion procedures suffer from a few disadvantages, although the worst one for conventional analysis (sample contamination from dissolution of the crucible) is not important for activated specimens. The most serious one in my opinion is that there is no clear end-point to the dissolution since the operator only becomes aware of the incompleteness of the procedure when he has dissolved the melt. Adding additional steps to complete the dissolution can be lengthy and troublesome.

2. *Organic Matrices*

Organic materials can be mineralized by a variety of procedures.

a. Dry Ashing. These methods range from simple heating in an open air oven to combustion in oxygen either under pressure in a calorimetric bomb or simply in a large flask filled with oxygen at normal pressure as proposed by Schöniger [10]. This last procedure seems particularly attractive for its simplicity and rapidity [11], and with special modifications even large samples (up to ten grams) can be rapidly mineralized [12]. Figure 1 shows a type of Schöniger combustion flask which has been developed successfully for use on large samples. The ignition is started by an external lamp, thus minimizing the risk of contamination during the combustion run.



1a Combustion apparatus

1b Ignitor

Figure 1. Schöniger-type combustion apparatus (1a) and ignitor (1b). 1. Sylvania DFC, DFN, projector lamp, 2. Amphenol 7854-type standard socket, 3. Plastic tubing, 1⅛-inch i.d., 7 inches in length, 4. Normally open type push-button switch, 5. No. 6 rubber stopper drilled to accommodate electrical wiring, 6. Electrical wiring. (Reproduced with permission from reference [12])

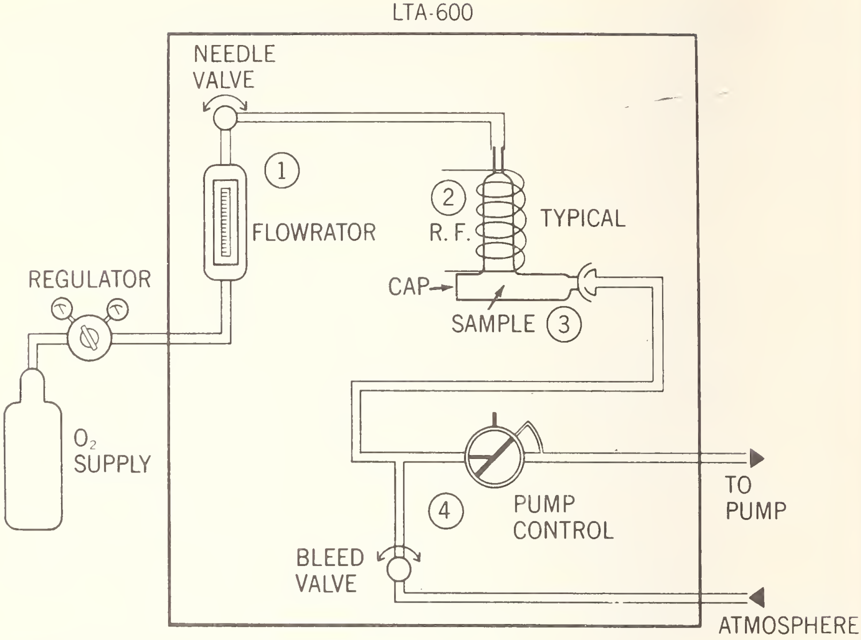


Figure 2. Diagram showing the principle of operation of the low-temperature excited oxygen asher. Commercial oxygen is admitted through a flowrator followed by a needle valve (1). It passes through the high-frequency electromagnetic field (2), which produces excited oxygen species which attack the sample in the oxidation chamber (3). Exhaust vapors are removed by a mechanical vacuum pump which is controlled by the exhaust valves (4). (By courtesy of Tracerlab West)

The use of excited oxygen at low temperature as proposed by Gleit and Holland [13] has resulted in commercial equipment in which mineralization of many samples can be attained simultaneously, and it has been used satisfactorily on activated specimens [14]. Figure 2 shows the principle of operation of the equipment. Major advantages of this technique are that only pure oxygen is the reagent used with no ignition device, and the destruction proceeds at temperatures of about 120–200 °C. The ash obtained should therefore be truly representative of the original organic samples, since contamination or losses should not occur. Therefore, the use of this technique seems particularly attractive for preirradiation ashing. The importance of this treatment should not be underestimated. The absence of organic matter, in fact, simplifies many irradiation problems, namely that of safety, by minimizing the risk of over-pressure during irradiation and risk of explosion during capsule opening.

A limitation of this technique is a rather low ashing rate (usually a few hours are required) which is largely dependent on the surface area of the sample. A preliminary complete drying of the samples is also required since the equipment must be operated under a 1 mm oxygen pressure.

b. Wet Ashing. This method has the advantages for activation analysis that were previously outlined for acid dissolution. An enormous amount of "recipes" is available, and indeed the problem here is how to choose well.

Standard procedures such as those recommended by the British Analytical Methods Committee [15] which were fully tested on a variety of matrices should be used first before trying short cut procedures for the actual samples. Recently, the use of 33% hydrogen peroxide seems particularly attractive [16,17].

c. Fusion Methods. These methods for organic materials are not employed frequently, but recently satisfactory application of the $NaNO_3$-KNO_3 mixture for the mineralization of biological materials has been reported [18].

III. Separation Techniques

A large variety of techniques is now being used for radiochemical separations. Together with improvements in well established techniques, new techniques are being studied. A trend seems to be to try to obtain the advantages of two different techniques by developing an "intermediate" technique. Thus, together with a few classical techniques such as precipitation, distillation, solvent extraction, ion exchange, and paper chromatography, other techniques whose names are not yet well established such as solvent extraction chromatography, reversed phase thin layer chromatography, *etc.* are now being proposed as possible tools for the radiochemist.

While many selective and rapid procedures undoubtedly can be obtained by that means, the literature situation tends to become confusing since it is often difficult to distinguish those that are better, from those that are different.

A. PRECIPITATION

The most classical technique used by the radiochemist is still very frequently employed with success, although the selectivity obtained is generally not high because of coprecipitation and adsorption reactions. The use of organic reagents as selective precipitants [19] has not yet been fully exploited.

The necessity of relatively large quantities of carriers to obtain precipitates with good yields often introduces difficulties in coupling precipitation with many modern techniques which are better performed with microgram amounts of material. The use of coprecipitation or adsorption on a preformed precipitate is a way of avoiding this difficulty.

B. SOLVENT EXTRACTION

This method is becoming one of the preferred tools by radiochemists. Very selective textbook procedures which although not specifically developed for radiochemical separations, can often be applied. The classical books by Morrison and Freiser [20] and Stary [21] are excellent reference sources for solvent extraction in general and for the extraction of metal chelates in particular, respectively.

The techniques involved are simple and rapid, and no special equipment is required. The partition coefficients are generally not very sensitive to variations in the concentration of the extractable complexes. Therefore, small amounts of carrier can be added to measure the chemical yield directly by colorimetric or spectrophotometric measurements on the organic phase.

Ion association systems although not highly selective, have the advantages of being carried out at high acid molarities. Therefore, they are ideal for preliminary separations, intended, for example, for removing a highly active component. A high selectivity is obtained through the use of chelating agents at controlled pH. The use of liquid exchangers such as long chain aliphatic amines is another way of achieving high selectivities. Sequential separation schemes based on solvent extraction are being reported recently for activation analysis purposes [22,23].

Reversed phase partition chromatography can be considered as a method for carrying out solvent extraction on columns and could find many new applications. The extractant is kept stationary on the column by adsorbing it on an inert support, such as cellulose powder, Teflon, Kel-F *etc.*, and the aqueous solution is passed through as in column chromatography. The review paper by Cerrai [24] deals extensively with the technical details.

C. DISTILLATION

Many elements can be simply distilled from the proper media either in the elemental state (halogens), or as halides (As,Hg,Sb,Se,Sn,Ge), oxides (Ru,Os,Ir), or as hydrides (P,As,Sb). Twelve elements can thus be distilled in a fairly quantitative way as bromides from sulphuric acid solutions [25], and an automated procedure for the separation of five of them has been reported [26].

Many separation schemes take advantage of a preliminary distillation step, [27-30]. Distillation for those elements to which it can be applied is certainly one of the best techniques since the purity of the separated fractions can be rather high. A careful design of the distillation equipment is essential to obtain quantitative transfer and good decontamination. Figure 3 shows a very efficient apparatus for the distillation of bromides of As, Hg, Sb, and Se from activated biological specimens. Details on the procedure are found in reference [26].

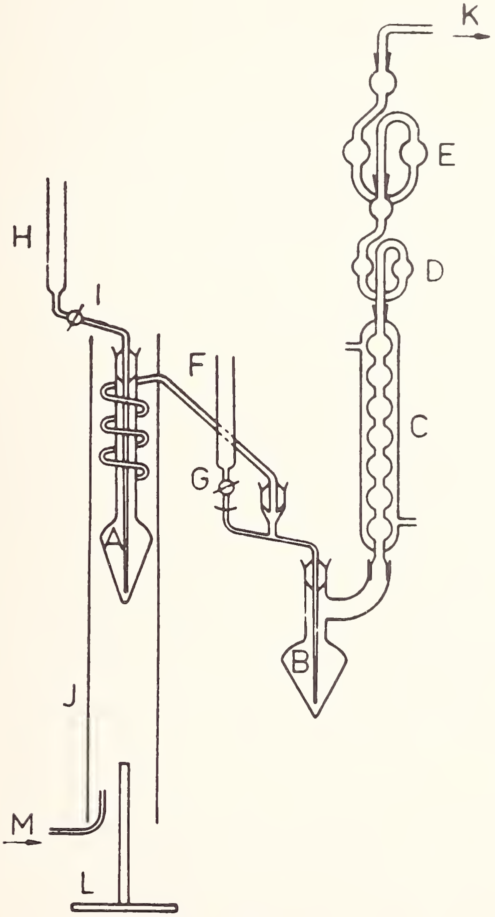


Figure 3. Apparatus for distillation of bromides of As, Hg, Sb and Se from activated biological specimens. A. Distillation flask, 15 ml volume, 175 mm long, B 14 joint, B. Receiver flask, 30-ml volume, 120 mm long, B 14 joints, C. Reflux condenser, 150 mm long, B 10 and B 14 joints, D., E. Traps for 2 and 5 ml, respectively, B 10 joints, F., H. Funnels, 10 mm x 100 mm, G., I. Stopcocks, J. Borosilicate tube, 45 mm x 380 mm, K. Arrow points to water suction pump, L. Bunsen burner, M. Compressed air. (Reproduced with permission from reference [26])

D. ELECTROCHEMICAL METHODS

Electrochemical methods have seldom been used in activation analysis. While electrodeposition is clearly not a selective separation procedure, the use of controlled potential electrolysis can afford a separation into groups by a stepwise increase in the deposition potential. The scheme proposed by Albert *et al.* [31) for the analysis of high purity copper is a classical example. A procedure of internal electrolysis has recently been reported for the determination of copper in high purity lead [32].

Electrophoretic focussing of ions, even though it is a very fast technique has found very limited application in activation analysis [33]. The major limitation is apparently the necessity of working with sample weights of the order of micrograms to obtain a neat separation of bands. This technique was found useful to separate carrier free isotopes from large amounts of interfering radioactivities, with decontamination factors of 10^5-10^7 [34].

E. ISOTOPIC EXCHANGE

Isotopic exchange on ionic crystals and amalgams is a well established technique, and procedures for at least 14 ions have been reported. See [35] and [36] for detailed references. The selectivity attained even if it is not outstanding, (frequently other elements are adsorbed by competing processes) is however sufficient for many practical applications, and the technique has the advantage of an extreme simplicity.

A limitation of the technique with ionic crystals is the fact that once the radionuclide has undergone isotopic exchange, it is difficult to add other steps to the radiochemical separation without redissolving the whole mass of exchanger. Amalgam exchange is more flexible since the amalgamated nuclide can easily be stripped from the amalgam into the aqueous solution.

The selectivity can be increased by the use of an appropriate stripping agent, and counting operations can be simplified since a correction for self-adsorption in the amalgam is no longer needed. A drawback is that amalgams cannot be stored for long periods.

Both techniques suffer from the impossibility of measuring the chemical yield, with any technique other than the radioisotope dilution method.

F. CHROMATOGRAPHY

1. Ion Exchange Chromatography

This technique is now a classical one for radiochemists, and many routine procedures are based upon it both for selective individual separations and sequential group separations. The field was recently received by Walton [37].

Detailed treatment of the principles of ion exchange is reported in the many books treating this subject. The classical book of Samuelson [38] refers particularly to analytical applications and deals extensively with technical details. The field is still under a vigorous expansion, particularly in those areas of the chromatography of metal complexes. The formation of metal complexes offers in fact a simple way of varying the sign and absolute value of the specific charge of the ion, and consequently of varying its behavior on ion exchange columns.

The formation of negatively charged metal complexes in the presence of high concentrations of strong ligand acids (HCl,HF) has resulted in many elegant classical procedures based upon the use of anion exchange columns. These procedures are the foundation of most sequential group separations (see below).

A trend here seems to be the study of ion exchange in aqueous solution to which organic solvents and eventually chelating agents are added. The effects obtained are rather complex since the hydration of ions decreases (and therefore the specific charge increases) and the formation of uncharged organic complexes is induced when chelating agent is added. Since both effects are different for different ions, the picture of the ion exchange behavior of a column can change completely. While most of these studies are still in the preliminary stages of studying the behavior of the ions [39-41], a few useful applications are already completed [42,43].

Optimization studies on the analytical operation of chromatographic columns also show promise for eliminating a few of the drawbacks of ion exchange resins such as the relatively long time required for a separation. A careful grading of the resins beads to minimize the differences of the bead diameters, has lead to a considerable improvement in the time required for sequential separation of ions [44].

2. *Paper Chromatography*

This is a technique frequently used for many years in activation analysis. In this technique, as in ion exchange, progress is being made *via* the development of hybrid techniques, such as chromatography on the paper strips impregnated with liquid ion exchangers [45].

3. *Thin Layer Chromatography*

This method retains the advantages of paper chromatography and adsorption chromatography. The adsorbent instead of being packed in a column, is layed on a glass plate, dried, and then treated as a paper chromatogram. It has the advantage that the time required to reach a good separation is usually much less than with paper. Thin layer chromatography is now finding its first applications in activation analysis [46,47]. A modification of thin layer chromatography, reversed phase thin layer chromatography, with TBP in the stationary phase has also been reported [48,49].

A common characteristic of these techniques is the necessity of using rather small samples to obtain a clean separation of spots. They seem therefore particularly suited to activation microanalysis.

4. Gas Chromatography

The possibility of using gas chromatography as a fast separation technique in radioactivation analysis has been explored only recently [50,51]. With this technique the sample is volatilized and passed into the gaseous form through a chromatographic column filled with a proper material and heated at a proper temperature. The interaction between the column and the gaseous phase is usually a partition process (gas-liquid chromatography) or an adsorption process (gas-solid chromatography). Different components of the gaseous phase are slowed at a different rate during the passage through the column and appear as separate peaks to the detector placed at the output of the column. A few minutes are usually sufficient to complete the chromatographic run. The detector can of course be a gamma-ray spectrometer, thus increasing the selectivity of the overall procedure, and other conventional detectors can be coupled to increase further the amount of information obtainable. Figure 4 shows a block diagram of a radiochromatograph-detector coupling system and details of the actual set-up which includes a fast transfer-injection system of the activated specimens, can be found in the mentioned references.

Gas chromatography which is highly developed in organic chemistry seems particularly attractive for extending this technique to metal chelates [52].

G. INORGANIC SEPARATORS

The use of inorganic materials packed into chromatographic columns and employed in the same manner as the organic ion exchangers is at its beginning in activation analysis, although considerable experience on a few materials is available from studies on the separation of fission products [53].

Inorganic materials can react with a solution of mineral ions percolating through the column by means of processes such as ion exchange, isotopic exchange, physical adsorption, mixed crystallization, precipitation and redox reactions. All of these processes can contribute to the retention of

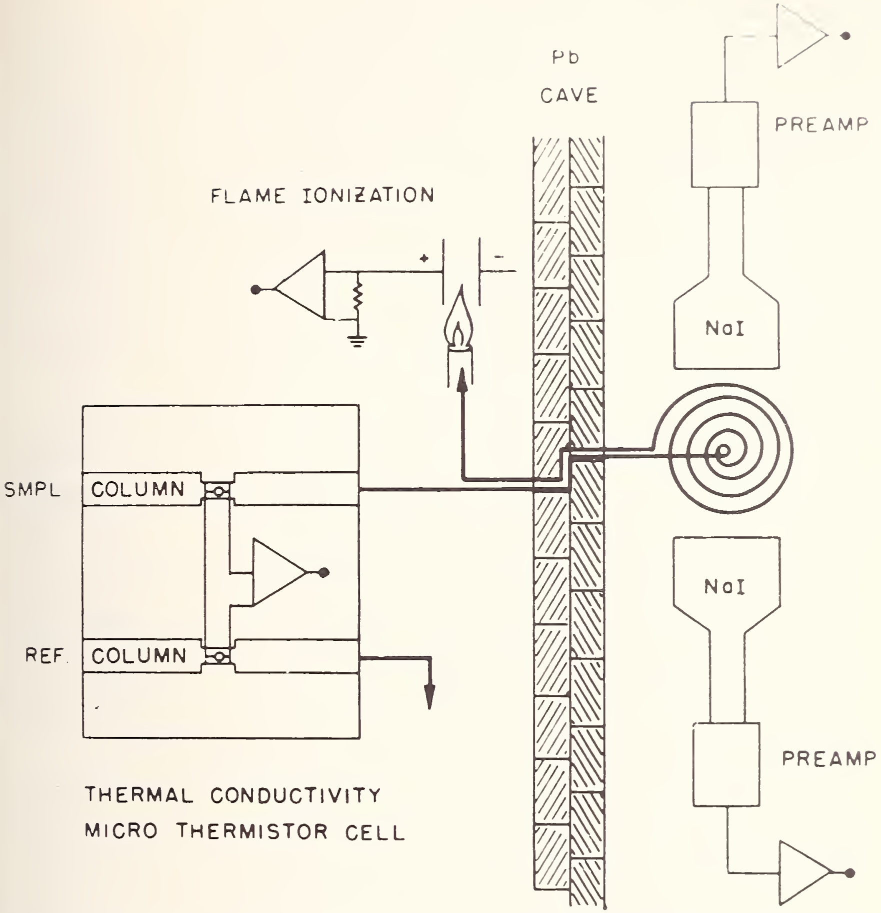


Figure 4. Block diagram of a radiochromatograph-detector coupling system. (Reproduced with permission from reference [54])

one or more ions on the column to a different extent. The complexity of the mechanisms involved makes it difficult to foresee the behavior of different systems, and it even makes it difficult to find a proper name for the material and process [35].

However, the effects of these "black boxes", whatever the way they work, are very interesting, and their advantages may be summarized as follows: (1) Extremely high decontamination factors can be reached in the removal of interfering radioactivities, (over 10^{10} in the removal of ^{24}Na on hydrated antimony pentoxide). (2) The availability of a large variety of materials which behave differently in the same medium makes it possible to obtain different separations starting with the same solution by just changing the kind of column and eventually using a few of them in series.

(3) The separations are fairly rapid since the column dimensions can be small (typical volume 2-3 ml) and the columns can be used with a fairly high flow rate (typically 1-3 cm^3/min.). (4) The reagents can be stored indefinitely and need no further pretreatment before use. Preliminary conditioning entails only washing the column before the adsorption step.

Our laboratory has been working on this subject for a couple of years with limited personnel and we hope that through the development of suitable separators it might be possible to simplify many analytical procedures, both by studying selective "filters" to strip one or two dominant radioisotopes from a solution and by studying schemes based on columns in series resulting in considerable decrease in time of separation.

Two separators have been studied in some detail, and the results of them have been already reported. Both of them are now available commercially. The first [54] is a substoichiometric form of manganese dioxide (MDO) which shows an excellent retention of ^{56}Mn with decontamination factors exceeding 10^8 from low acid molarities on columns heated to at least 60 °C. Figure 5 [55] shows the decontamination obtained on ^{56}Mn rich biological specimens. MDO is not selective for manganese and various applications are shown in the mentioned reference. The behavior of 60 ions on MDO has been determined from 0.1 M HNO_3. The behavior in four other media has recently been studied and the results will soon be reported.

The second [53] is a hydrated form of antimony pentoxide (HAP) which has shown an excellent selectivity for sodium from 12 M HCl with decontamination factors exceeding 10^{10}. Among 60 elements tested only tantalum was retained with sodium. Therefore, this material should find interesting applications in the biological field for removing ^{24}Na prior to high resolution gamma-ray spectroscopy, and indeed, preliminary results obtained in other laboratories after its use was first reported [35] are encouraging.

Figure 6 shows the application of HAP to the determination of K, Mn and Br after removal of ^{24}Na from irradiated blood, and Figure 7 shows its application to an urine sample. This last case clearly shows that a "black-box sodium separator", is not an answer to all problems in the biological field since often a desired radioactivity is hidden under another prevailing radioactivity *etc*. This also stresses the importance of an easy adaptation of the technique to actual samples when one wants to retain the full advantage of selectivity of the detector.

The behavior of HAP with seven other media has recently been studied and will soon be reported. Sodium is always retained but with less selectivity. This is a disadvantage when HAP is used as a selective filter, but on the other hand applications to other separations can be made.

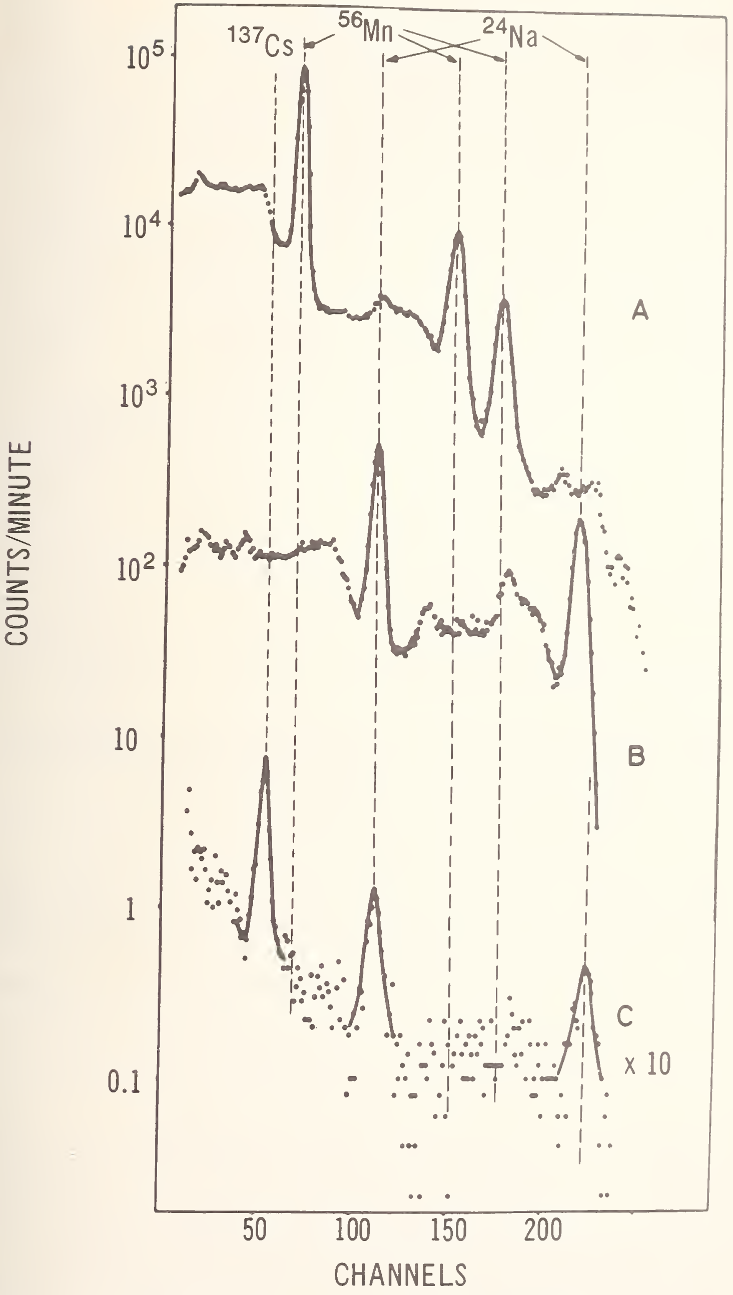


Figure 5. Decontamination obtained on ^{56}Mn-rich biological specimens. A. Before chemical separation. Trace quantities of ^{137}Cs have been added, B. After passage on an MDO column, C. After passage on an ammonium phosphomolibdate column.

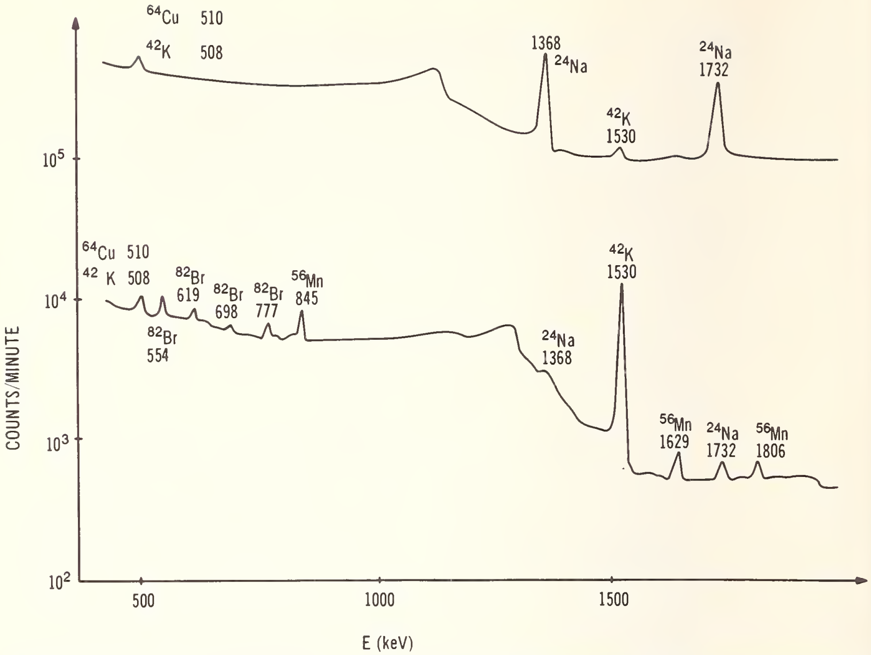


Figure 6. Results showing the use of HAP in the determination of K, Mn, and Br after removal of ^{24}Na from irradiated blood.

Other materials have been studied in a preliminary way, and the results obtained will be briefly reported in the experimental session.

IV. Separation Techniques for the Elements

The large number of radiochemical techniques available make a rather confusing situation for an unexperienced analyst who must develop a separation procedure for an analysis.

In this section an attempt is made to provide some general orientation on which technique seems best to separate a given element selectively. We do not refer to specific procedures unless they are rather unique, since they apply frequently to particular matrices and need adaptation in most cases.

Detailed procedures can be found in the Nuclear Science Series "The Radiochemistry of the Elements" [57] or in the book by Bowen and Gibbons [58]. The radiochemical purity attained through these procedures is frequently not necessary with the modern detectors and some "short-cuts" may be attempted. The judgment of selecting the best technique for each element is of course rather personal, but a personal judgment is perhaps better than a list of ten or fifteen techniques which are "applicable".

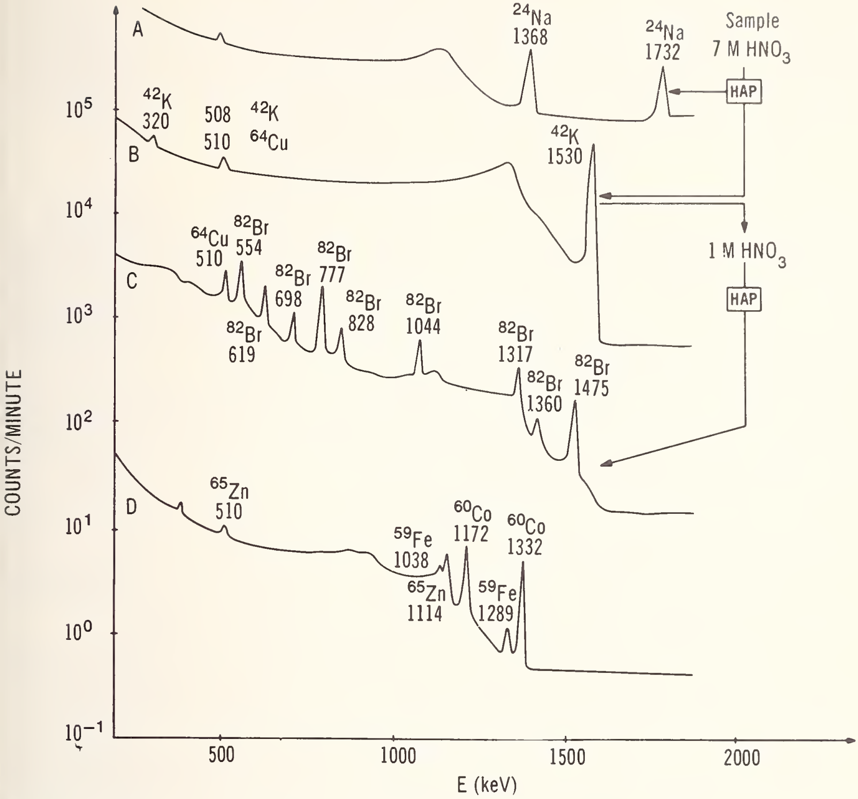


Figure 7. Results showing the use of HAP in activation analysis of urine (spectrum D is obtained from decay of spectrum C).

In suggesting a technique we assume that the radioisotope to be separated is formed by the (n,γ) reaction and is one of the most frequently used or "analytical" ones [59].

A. GROUP I A: NA, K, RB, CS

All these elements are not extractable with solvents in common systems, and this offers an easy way of removing them although not selectivity.

Ion exchange in mixed solvents can also be used for the same purpose [43]. Inorganic separators offer perhaps the best tool for the selective separation of the various alkali ions. A large amount of literature is available for the separation of fission-product cesium on inorganic exchangers [53], and the selective removal of sodium on HAP was already mentioned.

The fractionation of alkali ions on cation exchange resins in a classical procedure is lengthy and must be carefully optimized. Fractionation on inorganic separators seems less critical. Extraction chromatography has also been recently proposed [60].

B. GROUP II A: MG, CA, SR, BA

Again the whole group can be removed by taking advantage of its nonextractability in most common solvent extraction systems. Chemical separation of Mg is made difficult by the short half life of ^{28}Mg. Fast procedures involving isotopic exchange [61], and solvent extraction after preliminary purification [62] are reported.

A number of procedures are available for the separation of Ca, Sr, Ba, involving precipitation reactions, ion exchange on resins or inorganic materials, and isotopic exchange.

C. GROUP III A: SC, Y, RARE EARTHS

The high cross section of Sc make its determination rather simple with very little radiochemistry needed to remove interfering elements.

Yttrium and the rare earths are easily separated by precipitation as the fluorides, while solvent extraction affords a way of separating Y from the rare earths.

Separation of individual rare earths is a problem usually solved by ion exchange on which an enormous amount of literature is available. A procedure recently reported for activation analysis of lanthanides in sea water [63] is a classical example which includes preconcentration and removal of uranium before irradiation to avoid interferences from fission products. Rare earths are separated individually, and very high sensitivities are obtained.

However, it should be considered that the availability of Ge(Li) detectors diminish considerably the need for individual separation of the rare earths. In a mixture of rare earths with relative abundances in the range of the natural ones, 8 to 10 individual nuclides can frequently be distinguished without separation. Nondestructive determination of many rare earths in rock samples has even been reported [64].

D. GROUP IV A: TI, ZR, HF

The separation of titanium is a case similar to that of magnesium in which the combination of a low activation cross section with a short half life hampers its determination. Techniques of fast radiochemistry usually based on solvent extraction [62] allow a separation in about 10 minutes with good chemical yields.

Zirconium and hafnium also require in general chemical separations for their determination. Their behavior on anion exchange resins, particularly in HCl and HCl-HF mixtures offers many possibilities for their selective separation.

E. GROUP V A: V, NB, TA

Vanadium in spite of the short half life of its activated product can be determined easily (frequently nondestructively) due to its high activation cross section. Techniques for its radiochemical separation are usually based on solvent extraction.

Niobium also gives a short-lived radioisotope which usually requires chemical separation. Again, solvent extraction is the technique of choice because of its rapidity and selectivity.

Tantalum gives both a short-lived and a long-lived radioisotope; in general both require a radiochemical separation. Solvent extraction and adsorption on hydrated antimony pentoxide from 12 *M* HCl solutions [56] (as already mentioned) can both be satisfactory for the separation of tantalum.

F. GROUP VI A: CR, MO, W

A selective separation of Cr can be obtained by distillation as CrO_2Cl_2. Adsorption on MnO_2 has also shown sufficient selectivity for many practical applications [54].

Both Mo and W can be separated with good selectivity by anion exchange and solvent extraction.

G. GROUP VII A: MN, TC, RE

Manganese has such a high activation cross section that frequently, nondestructive analysis is sufficient to determine it, except in certain biological samples where extremely low abundances still have a definite biological significance. Inorganic separators were successfully applied to this problem [56].

Rhenium is not determined very frequently, but solvent extraction appears to be the best way of selectively separating it.

H. GROUP VIII: FE, CO, NI; RU, RH, PD; OS, IR, PT

Anion exchange procedures from HCl media are frequently used for the separation of Fe and Co. Solvent extraction is also a classical tool for the selective separation of iron, while precipitation techniques for Co and Ni with α-nitroso, β-napthol and dimethylglyoxime resp. are still among the best. It should also be noted that while the separation Fe-Co is essential in scintillation spectroscopy, both elements can frequently be determined together nondestructively in many materials, with the use of Ge(Li) diodes after decay of prevailing short-lived isotopes.

Ruthenium is an element with very low abundance, for which most classical methods fail or are exceedingly complex. Its determination by neutron activation requires chemical separation, and the distillation of RuO_4 appears as the most selective technique.

Rhodium gives only a short-lived nuclide, and fast radiochemistry is essential. Procedures by solvent extraction are reported which require only a few minutes.

Osmium can be simply distilled while complex and lengthy procedures usually involving many selective steps are required to separate Ir, Pd and Pt.

I. GROUP I B: CU, AG, AU

A wide variety of radiochemical techniques is available for the separation of these elements. Isotopic exchange is an easy technique for silver, and recently we noted that isotopic exchange of Cu on a CuS column is also a rapid way of separating Cu. Silver is very strongly retained by hydrated antimony pentoxide from any acid except HCl. Electrolytical techniques or spontaneous deposition on less noble metals can give rather selective procedures for these three elements.

J. GROUP II B: ZN, CD, HG

Zinc can frequently be determined nondestructively by Ge(Li) spectroscopy. Anion exchange from HCl of varying concentration allows individual separation of these three elements. Isotopic exchange with mercury and amalgams is also a good technique for them.

K. GROUP III B: AL, GA, IN, TL

The short half life of ^{28}Al increases the difficulty of its radiochemical separation. Procedures based on solvent extraction usually require about ten minutes. Nondestructive analysis is however frequently possible for aluminum in many matrices.

Anion exchange from HCl is a satisfactory procedure for Ga. Isotopic exchange on amalgams is used with good results on In and Tl.

L. GROUP IV B: SI, GE, SN, PB

Selective distillation procedures are frequently employed for both Si and Ge.

Anion exchange and solvent extraction procedures frequently apply to germanium and tin. Lead is not frequently determined by activation analysis, and the uncertain isotopic composition when radiogenic lead is present may introduce a very serious source of error.

M. Group V B: P, As, Sb, Bi

Phosphates are frequently determined by activation. Being a pure beta emitter, the separated product ^{32}P requires a good radiochemical purity, and precipitation techniques are frequently applied. Phosphates are very strongly retained by acid alumina. This technique offers a simple way of separating them, not only for their determination, but also for the removal of large quantities of ^{32}P which frequently interferes as a result of its intense bremsstrahlung in the determination by gamma-ray spectroscopy of elements with low energy gamma rays. Arsenic and antimony can be volatilized as bromides or hydrides, thus obtaining fast and simple separations. Bismuth is most frequently determined by measuring the alpha activity of the decay product of ^{210}Bi (^{210}Po), separated by volatilization or electroplating.

N. Groups VI B: S, Se, Te

Sulphur is frequently determined by measuring ^{32}P produced by the (n,p) reaction. The same separation procedures indicated for phosphorus can be applied.

Selenium can easily be distilled as the bromide, while tellurium can be separated by precipitation of the metal. Ion exchange and solvent extraction are also frequently employed for both elements.

O. Group VII B: Cl, Br, I

Distillation is a good technique for all of these elements. Chlorine and bromine can frequently be determined simply by nondestructive procedures. Solvent extraction of Br_2 or I_2 is also a simple and selective technique. The precipitation of silver halides is not very selective, but it is a simple way for determining chemical yields.

P. Group O: Ar, Kr, Xe

Techniques for their separation usually involve the evolution of gases (usually by melting the sample) in a vacuum line, and fractional adsorption and desorption at low temperature on columns of activated charcoal or molecular sieves.

V. Separation Schemes

Activation analysis is certainly a technique which can determine many elements in a single specimen in a systematic way. Although in some cases a careful choice of irradiation and decay times, and availability of high resolution detectors can lead to the possibility of determining a large number of elements nondestructively [65], it is usually necessary (and in many cases even simpler) to devise a chemical separation scheme. At least 15 different separation schemes excluding successive modifications of a scheme have been reported in the last four years to separate 10 to 50 elements into groups [11,27,31,66-75].

The criteria with which the separation schemes were developed vary from case to case depending on the nature of the material to be analyzed, the selectivity of the detectors available, and undoubtedly, the author's preference of one technique over the other.

Some authors separate radionuclides into a few groups, leaving the detector to provide the final discrimination. Others separate radionuclides almost individually, and use the selectivity of the detector to verify the radiochemical purity.

The first approach certainly requires less effort in the chemical laboratory, but the risk exists that one radionuclide with an intense activity completely masks the others in the group. Therefore, a similar composition from sample to sample is required, and care should be taken to extend these schemes to different matrices. The second approach is more time consuming (both in the chemical laboratory and in the counting room), but it gives a higher sensitivity and less work is required to adapt it to different matrices.

Ion exchange is the basis of many of the reported schemes. The separations are generally based on sequences of adsorption-elution cycles on different resins and from different media. An exception is the scheme developed by Samsahl *et al* [75]. This scheme (Figure 8) is in fact based upon selective adsorption on columns in series. The medium is adjusted to that required for selective adsorption of each group by mixing the output stream from the preceding column with a suitable solution before entering into the next column.

This is a way of reducing the time of the entire adsorption-elution cycle to that of the first adsorption-washing step. The same technique could certainly be applied to other separation schemes based on ion exchange resins if a high speed of separation is essential. The scheme has been fully automated, and a commercial machine based on its principle should become available in the future.

Solvent extraction is perhaps not well suited to sequential separation of individual nuclides, but group separations can be obtained simply by

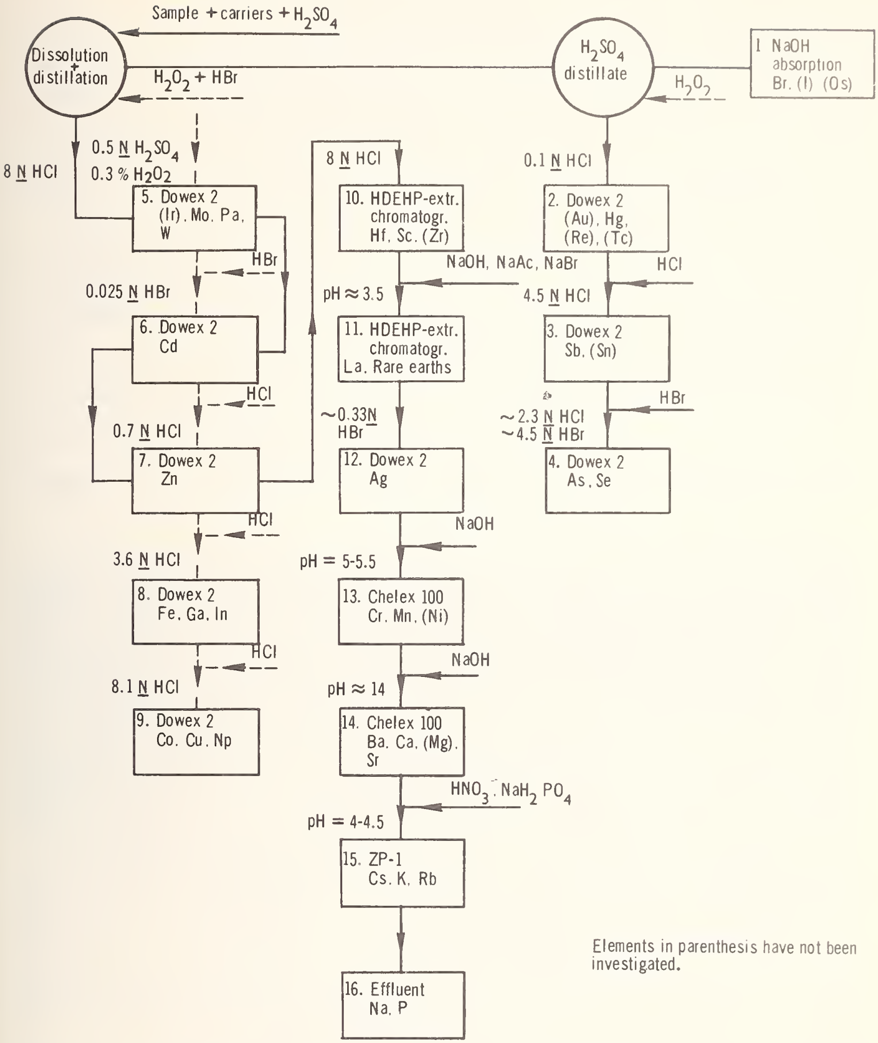


Figure 8. Flow diagram of separation scheme using selective adsorption on columns in series. (Reproduced with permission of Baker, Brooke, and Goode [23].)

successive extractions, after addition of buffers between the extractions to adjust the pH at the required levels. Thus a separation into six groups followed by scintillation spectroscopy and computer least square fitting of the output data lead to the determination of 22 elements in glass fragments for forensic analysis [23]. Figure 9 shows a flow sheet of the scheme.

Adjudgment of which approach is best and which scheme is best is obviously impossible since the choice should depend on the counting

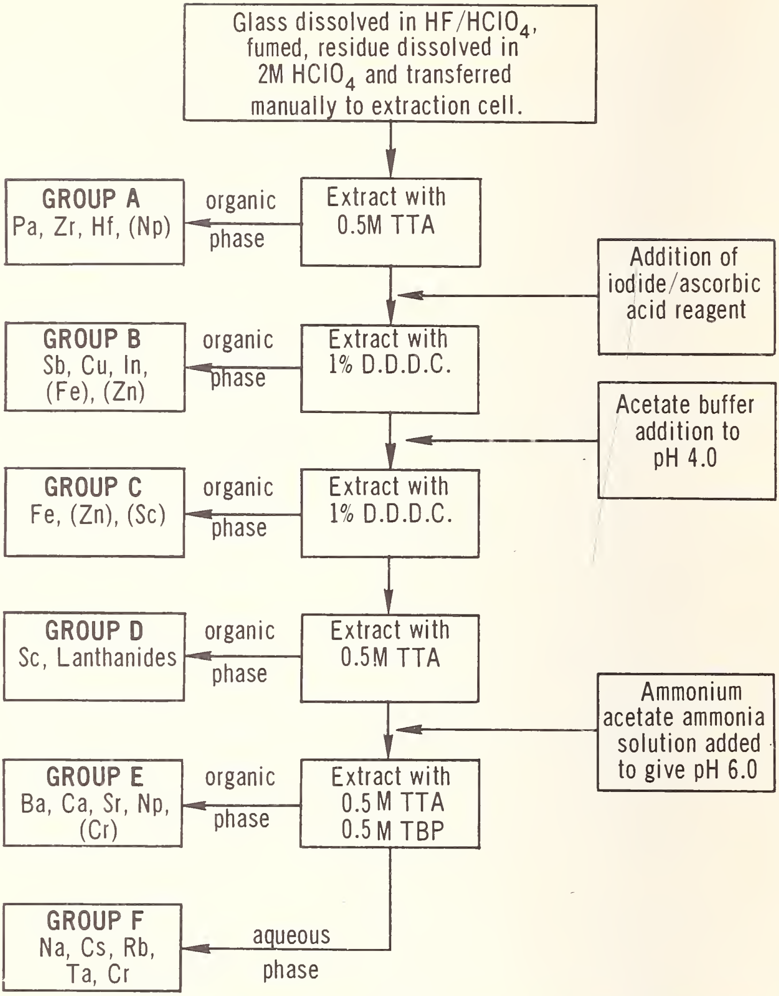

Glass dissolved in HF/HClO4, fumed, residue dissolved in 2M HClO4 and transferred manually to extraction cell.
Extract with 0.5M TTA
organic phase
GROUP A Pa, Zr, Hf, (Np)
Addition of iodide/ascorbic acid reagent
Extract with 1% D.D.D.C.
organic phase
GROUP B Sb, Cu, In, (Fe), (Zn)
Acetate buffer addition to pH 4.0
Extract with 1% D.D.D.C.
organic phase
GROUP C Fe, (Zn), (Sc)
Extract with 0.5M TTA
organic phase
GROUP D Sc, Lanthanides
Ammonium acetate ammonia solution added to give pH 6.0
Extract with 0.5 M TTA 0.5 M TBP
organic phase
GROUP E Ba, Ca, Sr, Np, (Cr)
aqueous phase
GROUP F Na, Cs, Rb, Ta, Cr

Figure 9. Flow diagram of group separations by successive extractions. (Reproduced with permission of Baker, Brooke, and Goode [23].)

facilities available and the problem to solve. It should however be noted that all of these schemes rely on NaI(Tl) scintillators for the final radioactivity measurement. The use of high resolution Ge(Li) detectors can bring substantial simplification for multielement determinations although other complications are introduced as seen later.

VI. Automation

Automation of radiochemical separations has been studied for the past few years in various laboratories (including ours) as a possible answer to the problem of doing destructive analyses economically on a large number of similar samples. Different machines have been built and used with success by the laboratory who designed them, and although none is yet available commercially, at least two of them should be very near to commercial production. The machines developed are based on various working principles, and an attempt to classify and review them is given below.

A. FIXED PROGRAM MACHINES

These machines are built to automate one chemical separation. They are therefore optimized for each particular job, and the program is built-in. The machine developed by Samsahl to automate the separation scheme of Figure 8 is shown in Figure 10, and is the best example of this category of machine [75]. The lack of flexibility of fixed program machines is compensated by their simplicity. They can also be quite compact (the mentioned machine is contained in a box with dimensions 50 cm × 30 cm × 30 cm).

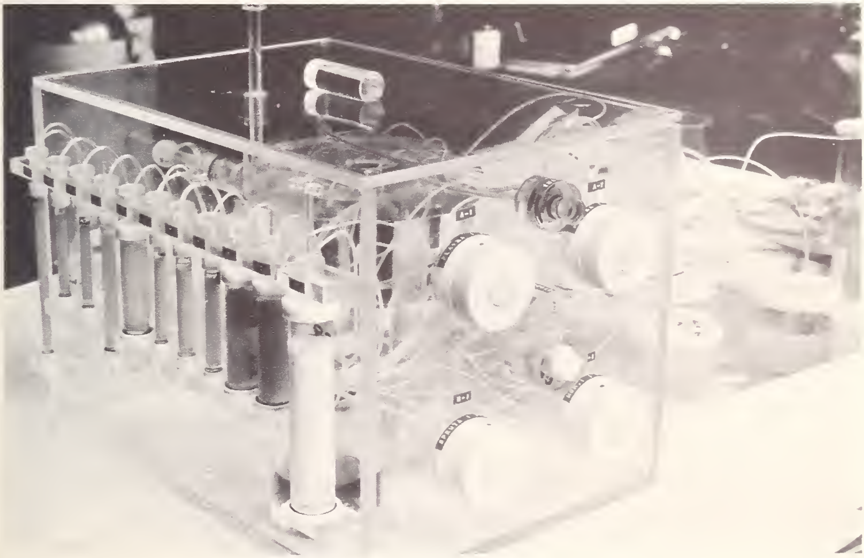


Figure 10. Fixed program machine used for the automation of the separation scheme shown in Figure 8. (Reproduced with permission of Samsahl, Webster, and Landstrom [75].)

B. PROGRAMMABLE MACHINES

In these machines the sequence of operations can be programmed so that the same machine can be applied to different chemical separations. Flexibility is of course their main advantage, which is counterbalanced by a higher complexity and cost.

They are based on the use of programmers which send the appropriate instructions to the various parts of the chemical machine generally in form of voltage levels which actuate the power relays of the different units (pumps, stopcocks *etc.*). (It is well to separate the programmer from the chemical apparatus to minimize contamination and corrosion of the electrical parts.)

Different kinds of programmers have been used which range from standard electro-mechanical ones [76], to more complex ones based on programming matrices [35] or magnetic tapes. This last type [23], called "continuous audiostone programmer" seems particularly attractive for use in the chemical laboratory. Here a series of audiofrequency tones are recorded on a standard tape recorder and each frequency is coupled *via* a low frequency band pass filter to an electronic switch controlling the external apparatus. The filter network can be converted by manual switching to a tone generator and in this mode can be used to make its own program by manual control of the various operations required for automation. The advantage of this apparatus, which should soon be available commercially from a British manufacturer, is the ease with which complex programs can be recorded and modified if required.

With respect to the different chemical units which can be connected to the programmers, they need to be especially developed for each separation technique. The problems involved are not too important, however. A solvent extraction cell for use with solvents heavier than water, which is used with the audiostone programmer automates the scheme of Figure 9 and will be available commercially.

A common requirement to all programmable machines is a reagent dispensing system to assure a correct delivery of the wanted quantities of reagents with the desired flow rates. These can be controlled by a pumping system (frequently of the peristaltic type) [77] or simply by gravity feed through long capillary tubes, while the quantities are usually time controlled.

The time required to run a chemical separation with these machines is generally somewhat shorter than that employed by manual operation, but of the same order of magnitude. When many samples are available a time advantage can be obtained by connecting many parallel units to the programmer.

C. Composable Machines

An intermediate approach is that of composing machines from modular units, each doing a certain step of the separation with a fixed program. This approach was the basis of a machine built in our laboratory a few years ago [78], and was applied to a few problems on analytical specimens.

D. Machines for Continuous Analyses

The principle of doing a chemical separation by moving the sample along an "analytical line" and submitting it to the different separations required at fixed points on the line (a sort of "assembly line" for analytical chemistry) had a great success in conventional analysis (particularly colorimetry).

In radiochemical separations for activation analysis, the machine developed by Comar [79] is a well known application of this principle. Recently substoichiometric separations based on the same principle have been proposed for the determination of mercury by radioisotopic dilution [7].

E. The Contamination Problem

Losses by adsorption of radioactivity on the parts of the machine which come into contact with the radioactive solutions must of course be avoided by a careful choice of materials.

Inert plastics such as polyethylene or fluorinated hydrocarbons are extensively used, and the market now offers a wide selection of tubes, manifolds, and valves, *etc.* which simplify the assembly of the "chemical" parts of the machines.

An advantage of programmable machines in this respect is that the program can include as a final step prior to reset an exhaustive wash of the "hot" lines. Continuous machines cannot be cleaned as well, although a false sample composed of a wash solution can be put between real samples in the sample changer which control the inlet to the analytical line. The machine would execute a complete analysis on the washing solution to provide a control. However, the number of analyses per unit of time is thus halved.

VII. Development Trends

In the introduction of this review, the opinion was expressed that the available radiochemical techniques and procedures are not well suited to present needs of radiochemical separations. The idea was also raised that a "new radiochemistry" could perhaps be developed, to meet present and presumably future needs in a more efficient way.

In this part an attempt is done to analyze present difficulties in a more detailed way, to suggest possible solutions, and review a few "first steps" done towards them in different laboratories.

A. THE EXISTING PROBLEMS

To see what the problems are let us follow an analyst who is facing a new problem on which he has no previous experience. There is no doubt even among the most dedicated radiochemists that a nondestructive determination when possible is preferable to a destructive one for many reasons.

Therefore, on any new problem the analyst will first make one or a few nondestructive trials. Should these trials fail, the next step will be dissolve the sample and make a radiochemical separation. I have already spoken of the difficulties associated with the three words "dissolve the sample", and I shall not dwell upon this point.

Once the sample has been dissolved, the question could be raised whether it is better to do as little chemistry as possible or to do some more chemistry and use a simpler detector system. The answer to this question is not easy. Physicists certainly prefer the first approach, while some chemists might prefer the second one. Whatever the personal preferences of the analyst are, he will probably make a preliminary literature search to see if a suitable chemical procedure already exists.

The results of this investigation will be most often discouraging, and indeed after a few of these investigations the analyst might decide to skip this step entirely. What he will find is in fact almost invariably a redundant procedure. This is not surprising when one takes into account the present rate of development of detectors and computer techniques and the time required to publish a paper. A redundant procedure can of course be used as such, and our analyst might decide to do a trial on the basis of a reported destructive procedure.

Here a new problem presents itself—the problem of reagents. Solutions of reagents cannot be stored indefinitely as transistors or condensers. Apart from real alteration of the reagents, an analyst would lose confidence in the content of a bottle which is standing on the shelf for a long time. Also a reagent may have been used frequently enough to make the suspicion of alteration seem reasonable.

The analyst must therefore prepare the necessary reagents. If special reagents are required which are not usually kept in stock, he must order them and await their arrival. Unfortunately this last situation is becoming more and more frequent, as selective separations call for special reagents which are not in general stock items.

After this obstacle has been overcome, the analyst is now ready to repeat a reported procedure exactly. Here is a new obstacle—while an electronic scheme can be copied with all guarantees that the copy will be identical to the model, the same is not true for radiochemical separations, as there are too many variables which cannot be precisely controlled:

purity of reagents, small alterations with time or exposure to light, small variations of the behavior of different batches of the same reagent *etc.*

At this point the situation might still be restored by making small alterations in the procedure by trial and error. To do this, the analyst must make good use of his "chemical feeling" which comes from his previous experiences and it therefore varies between individuals.

Let us suppose, on the other hand, that the analyst decides to develop an entirely new procedure, either because the reported ones are really not adaptable to his problem or because he feels he can do a better job by applying novel techniques. In this case his literature search changes direction, and he will therefore try to get from the reported papers on novel techniques as much data as possible to minimize the experimental developmental work.

Here he will find a rather confused situation. The fundamental techniques he has at his disposition are already many as was seen in section 3, and they tend to proliferate and to hybridize. This is a kind of proliferation which is certainly not dangerous, but authors suggesting a novel technique should perhaps not stop after the pleasant part of the job, that of giving a few typical examples, but also do the unpleasant part of it, the clarification of the behavior of most elements when the novel technique is applied. Again the analyst will be guided in the forest of old and new techniques by his "chemical feeling", and will come up with a new procedure which will become another tree of the existing forest.

I have of course deliberately exaggerated the difficulties of our poor analyst, but certainly his task is not simple. I leave to the audience the judgment on how this situation compares with the one existing in the field of detectors and instrumentation, and how present radiochemistry fits the present needs. Perhaps you will agree with me that what is needed is something more than a new scheme or a new technique, perhaps it is a new approach to the problem.

B. Ge(Li) Detectors and Radiochemistry

High resolution Ge(Li) detectors have certainly increased the possibility of nondestructive analysis, thus eliminating many problems for the radiochemist. In those cases in which a radiochemical separation is still needed, it is not certain whether the replacement of a NaI(Tl) detector with a Ge(Li) one is always advantageous, apart from considerations of sensitivity of detection which are clearly in favor of the former.

When one or just a few elements must be systematically analyzed in many samples, it is perhaps easier to develop a chemical separation scheme which selectively separates that element (or those few elements) thus solving the problem once and for all. The scintillation detector would in this case be sufficient.

Conversely, when a large number of elements need to be determined, that approach can be rather time consuming, and one would certainly prefer to take advantage of Ge(Li) detectors to minimize the number of groups to be counted.

The danger of this last approach is that once this scheme has been set up, let us say with 6 elements per group, as an example, when one of these elements is prevailing, the other five cannot be determined. The scheme can therefore be highly economical on typical cases, but it can also lead to analytical reports with a certain number of "not determined". This can perhaps be accepted in some problems, but for others, in which a correlation of the concentration of elements between various samples is needed (a problem typical of environmental and biological sciences), the lack of one figure can make meaningless all the other analytical data. In this case the analyst will be forced to proceed to a more complete chemical separation (if the sample is still in a condition to be further processed) or start all over again on a new sample. A long delay in the delivery of the final results may be the consequence.

To make a separation *ad hoc* for that unhappy sample is not a simple task at all, and the analyst will certainly regret for not having used the old schemes and the old detectors. As previously indicated, all of the available sequential separation schemes were made for the scintillator detectors. When developing new ones for the semiconductors, these problems should be considered.

Typically such a new scheme could be a sort of "binary sequential scheme" in which the elements are first split into two groups which in turn can be split into two other groups and so on, until even an individual separation of elements is achieved. The essential feature of this hypothetical scheme should be that each separated group is in such a form to be either counted or used as the input stage of the next separation step.

This "binary" scheme would be of general applicability, but as such, it is not optimized for any problem. Other schemes could be developed based on similar principles in which the number of elements and the disposition of elements in the various groups are optimized for the most typical samples. These schemes could be developed with the present knowledge of radiochemical techniques by the usual approach of trial-and-error.

A new method which might be investigated, is to take a Ge(Li) spectrum first, thus obtaining all the possible information (if one is fortunate, he might be able to determine even 8 or 10 elements in one spectrum), and afterwards selectively remove those elements, take a second spectrum, and so on until a clean background is obtained. This procedure could be called "chemical spectrum stripping," in analogue with instrumental spectrum stripping. Figure 11 shows an example of chemical spectrum stripping carried out on long-lived radioelements, in which an initial Ge(Li) spectrum allows the determination of Zn,Fe and Co. These are stripped out in one step with an antimony pentoxide (HAP) column from 1 *M* HNO_3, thus leading to the measurement of the underlying radioactivities of ^{85}Sr, ^{134}Cs, ^{46}Sc, and ^{86}Rb.

Another example is given by Figure 12, to show that this approach which would seem at first rather lengthy, could also be applied to short-lived radioisotopes. The irradiated sample (a fish muscle) initially results in the measurement of ^{24}Na, ^{42}K and ^{56}Mn by high resolution spectroscopy. To remove these radionuclides the sample was dissolved in 7 *M* HNO_3 and passed onto a column containing Sb_2O_5 and Al_2O_3. The first retains ^{24}Na and ^{42}K, while the second was added to retain ^{32}P, which was thought to be present in a sufficiently high amount to cause an interference after the separation of ^{24}Na and ^{42}K. The solution was then diluted to 0.1 *M*, and passed onto a MnO_2 column to retain ^{56}Mn. The resultant solution is measured by high resolution spectroscopy and allows the identification of ^{81m}Se, ^{134}Cs, ^{27}Mg, ^{87m}Sr, ^{69m}Zn, and ^{139}Ba.

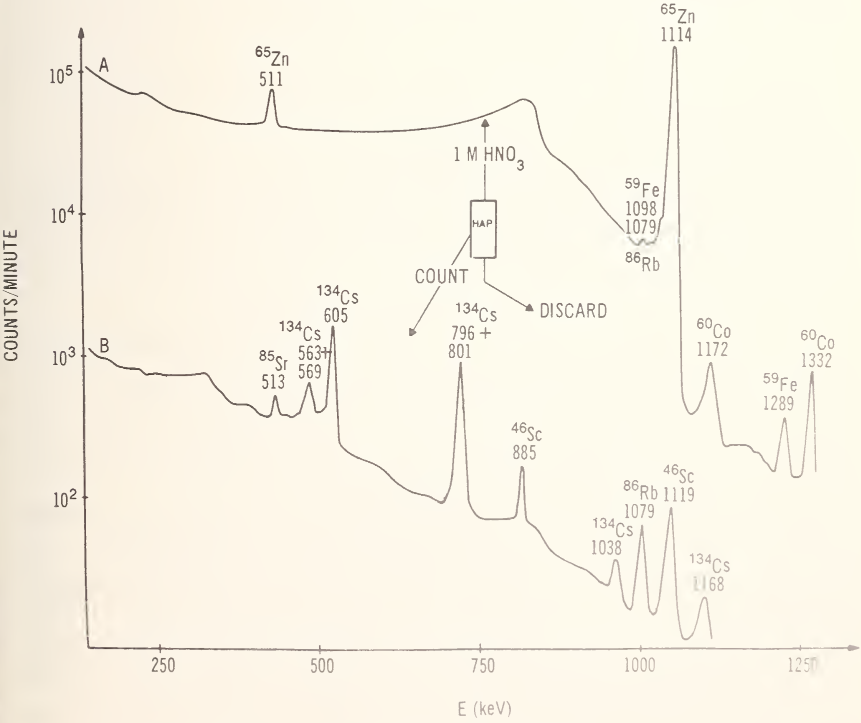


Figure 11. Example of chemical spectrum stripping applied to long-lived radioelements.
A. Gamma spectrum of the irradiated sample.
B. Gamma spectrum of the HAP column after separation.

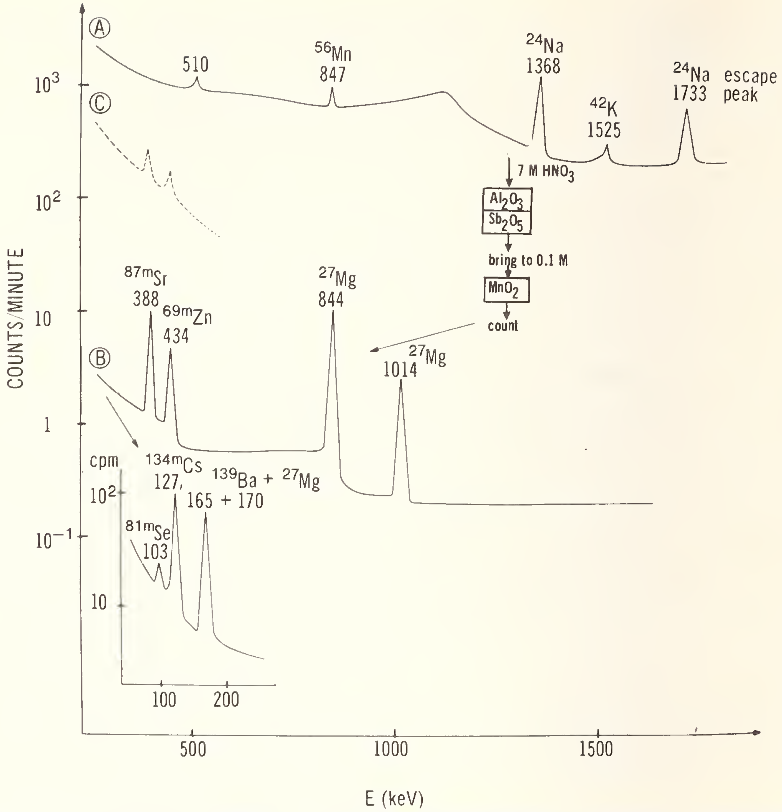


Figure 12. Example of chemical spectrum stripping applied to short-lived radioelements (The dotted spectrum C would be obtained in absence of the Al_2O_3 column).

A. Gamma-ray spectrum of the irradiated sample.

B. Gamma-ray spectrum of the effluent after the chemical separation indicated in the figure.

C. Gamma-ray spectrum of the effluent omitting the Al_2O_3.

The use of "chemical spectrum stripping" cannot be exploited fully at present since the choice of a radiochemical separation scheme is still a time consuming task, and it is perhaps still preferable to treat all the samples in the same way, even if it is not as efficient as treating each individual sample in a different optimized way.

The introduction of on-line computers in activation analysis, of which various examples are reported at this conference, will permit a fast processing of gamma-ray spectra, thus helping in the rapid assessment of which nuclides need to be removed for each individual sample. What is still needed is a way of deciding rapidly what to do to remove them. However progress is being made in this direction, and we hope that the day is not too far when the same computer which tells us what needs to be removed, will also tell us how to do the job.

C. RADIOCHEMISTRY AND ELECTRONIC COMPUTERS

To reach that ideal state of adaptation of radiochemistry to both the selectivity of the detector and the nature of the sample much work is of course needed. A few laboratories are presently exploring the field, and it is perhaps worthwhile to give at least an idea of the work under way, even if it is much too early to speak of results obtained.

1. Preparation of Input Libraries

Attempts are being made to find a way of presenting and recording the parameters which control the behavior of elements in different chemical systems in a way which is computer compatible. Thus the Radioelements Application Section of the Nuclear Center of C.E.A. at Grenoble (France) is assembling on punched cards all of the reported distribution coefficients of elements on ion exchange resins in a normalized library. Data from different authors are normalized to make them directly comparable between each other.

At the University of Ghent (Belgium), curves of distribution coefficients *vs.* acid molarity in ion exchange systems are being fitted to second order equations of the type $\log K_d = A + B\,(\mathrm{mol}) + C\,(\mathrm{mol})^2$, to determine the parameter A, B, and C which describe the behavior of an element in a given system.

At the author's laboratory the behavior of ions on inorganic separators is classified into one of three groups, depending upon whether the ion is completely retained, or partially retained or completely eluted in a standardized adsorption run. The form in which the data are collected and reported is of course strictly correlated to the way in which the laboratory intends to use them. At this preliminary stage of the work all possible ways should be explored. Later some sort of unification will be needed, but this should not be a difficult problem.

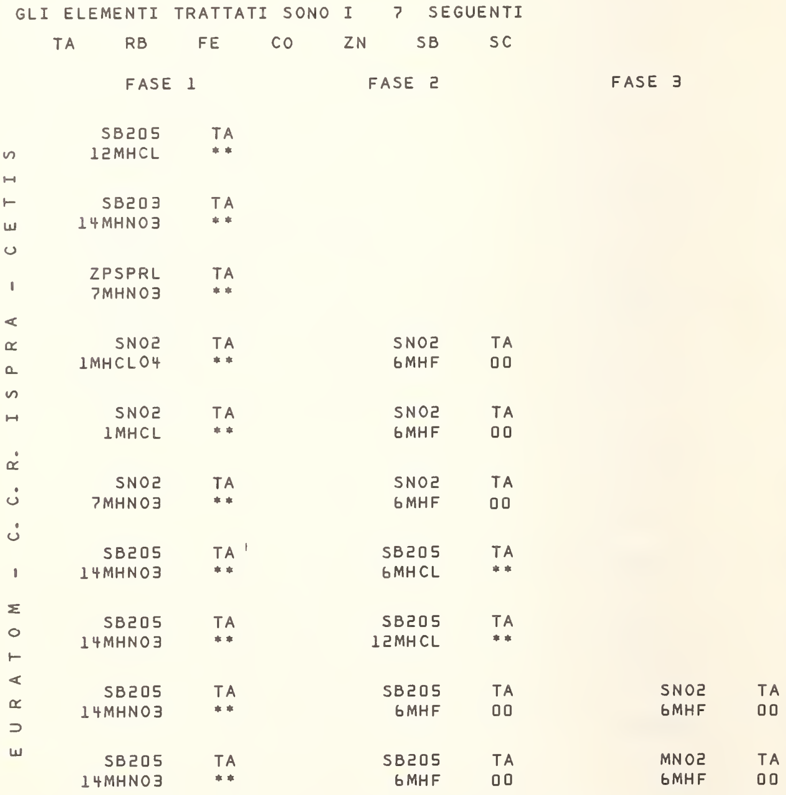
2. Computer Programs for Radiochemical Separations

When this standardization and classification work has been carried out, an attempt can be made to develop computer programs for radiochemical separations. These must of course be uniquely based on experimental data and chemical laws since the computer does not have that "chemical feeling" which is so important in developing procedures based on the trial and error approach.

The philosophy and aim of each computer program presently under development is somewhat different, and important modifications will certainly take place while the work is still proceeding. At Ghent University the program under development determines the conditions for separation of elements which show in a given system a sufficiently different behavior to make their separation possible without an optimization of the separation conditions. Simplicity and rapidity seem to be the primary goal at present. At Grenoble the optimization of the separation conditions is being studied, *i.e.* choice of the best medium and concentration to obtain a certain condition for separations by chromatography, eventually with an elution gradient etc.

In its present version, our program is capable of listing all possible sequences of standardized passages on inorganic separators which lead to the separation of one element from other given elements.

Figure 13 shows the output of the program in the case of the separation of tantalum from six suspected interferences in gamma-ray spectroscopic measurements (Rb,Fe,Co,Zn,Sb,Se). Extensions of the program for the development of group separation schemes and for choosing the most selective procedure for other problems are being worked out. Control



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GLI ELEMENTI TRATTATI SONO I   7  SEGUENTI
    TA     RB     FE     CO     ZN     SB     SC

         FASE 1                   FASE 2                   FASE 3

       SB205    TA
      12MHCL    **

       SB203    TA
     14MHNO3    **

      ZPSPRL    TA
      7MHNO3    **

        SNO2    TA                  SNO2     TA
     1MHCLO4    **                  6MHF     00

        SNO2    TA                  SNO2     TA
       1MHCL    **                  6MHF     00

        SNO2    TA                  SNO2     TA
      7MHNO3    **                  6MHF     00

       SB205    TA                 SB205     TA
     14MHNO3    **                 6MHCL     **

       SB205    TA                 SB205     TA
     14MHNO3    **                12MHCL     **

       SB205    TA                 SB205     TA                  SNO2     TA
     14MHNO3    **                  6MHF     00                  6MHF     00

       SB205    TA                 SB205     TA                  MNO2     TA
     14MHNO3    **                  6MHF     00                  6MHF     00
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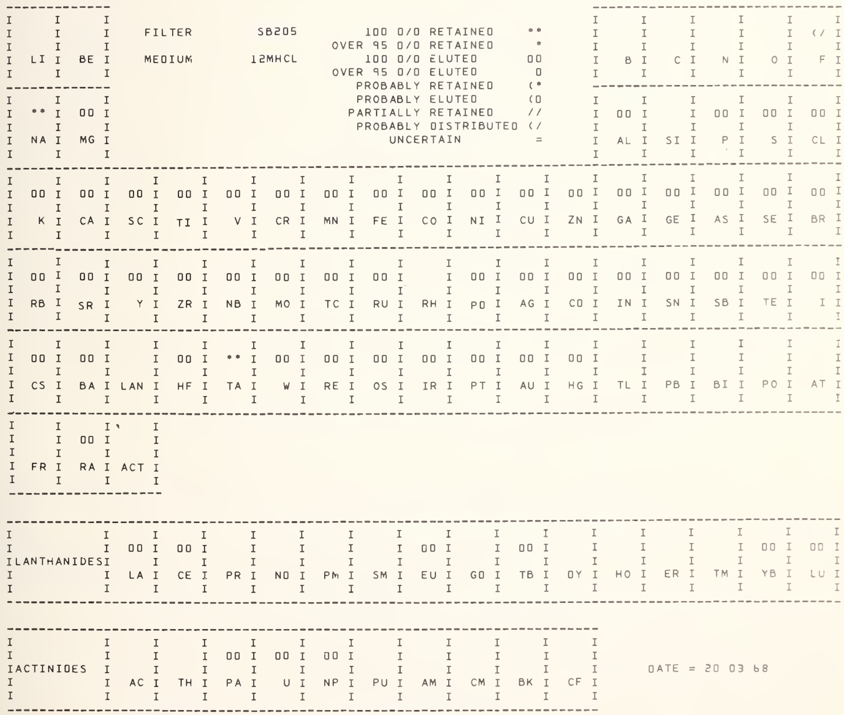
Figure 13. Computer program listing the separation of tantalum from six suspected interferences in gamma-ray spectroscopic measurements.

experiments are performed to determine which additional parameters can help to choose the preferred solution among many possible ones.

The particular feature of our way of building up separation schemes by addition of standardized operations, with no attempt to optimize within the operations, results from a desire to explain what might result from applying criteria typical of the development of electronic instruments. An electronic system is in fact made up from the combination of units, each performing a certain operation in a standardized way, which is indicated by the various characteristic curves which are shown in the catalogues. No one would ever think of building his own transistor, even if by that means one could perhaps make up the desired electronic scheme with less transistors or condensers. Similarly, a chemical procedure could be performed by combination of standardized steps, provided the characteristics of the steps (behavior of all the elements in that step, input requirements to the step, output of the step, *etc.*) are known. Figure 14 shows a first attempt of such a "characteristic sheet". At present we have provided for seventy of these standardized steps, with which already a good deal of chemistry can be done.



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I     I     I                            OVER 95 0/0 ELUTED        0   I     I     I     I     I     I
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Figure 14. "Characteristic sheet" providing known characteristics of standardized steps in chemical procedures.

While all these studies are done at present with chromatographic techniques (be it organic ion exchangers or inorganic separators), there is no apparent reason why a similar methodology could not be applied to other techniques such as solvent extraction where a good deal of data are available, and I hope that someone will soon undertake this task.

It is much too early to say what might come from all of these studies, but there is at least a reasonable hope that computers can be of help in the chemical laboratory as they are of help in the counting room.

3. Automation and Electronic Computers

The construction of machines to perform chemical operations automatically is the third step towards a new radiochemistry, and as I have already shown this step is perhaps more advanced than the two first steps. The availability of commercial machines is of course extremely important since it will enable laboratories with minor engineering abilities to enter the field with a good start.

All present machines are built for a large number of samples since the preliminary set up which is usually time-consuming, can only be justified in that case. This immediately eliminates a large number of activation analysis applications, dealing with small numbers of samples and perhaps prevents taking the highest advantage of Ge(Li) detectors. However, I would not consider this as a very severe drawback since once a computer has been "taught" to prepare the chemical separation scheme, the effort for translating it into a program for the automated machine seems a minor one. It would even seem that the computer could control directly the automated machine, and therefore, not only decide which is the best chemical separation, but also to execute it. The construction of such a sophisticated system cannot perhaps be justified at present on a practical basis, but certainly the field is open to research and development.

D. New Techniques in Radiochemistry

To speak of new techniques in radiochemistry might seem in bad contrast with what I have said in the preceding sections, but while their need is certainly not vital, this does not mean that the search for simpler techniques of radiochemistry should stop. Less conventional techniques could in fact be a way of skipping over many existing problems.

Thus, even if the present procedures of sample dissolution should be standardized, well controlled, and perhaps even automated, this step will still remain an unpleasant part of the radiochemical procedure. Here new techniques could perhaps be studied, such as direct volatilization of elements by heating the sample at a high temperature in presence of suitable gaseous reagents [80]. The number of elements which can be volatilized below 350 °C is indeed high, and Figure 15 from reference [81] summarizes the existing knowledge in an excellent condensed way.

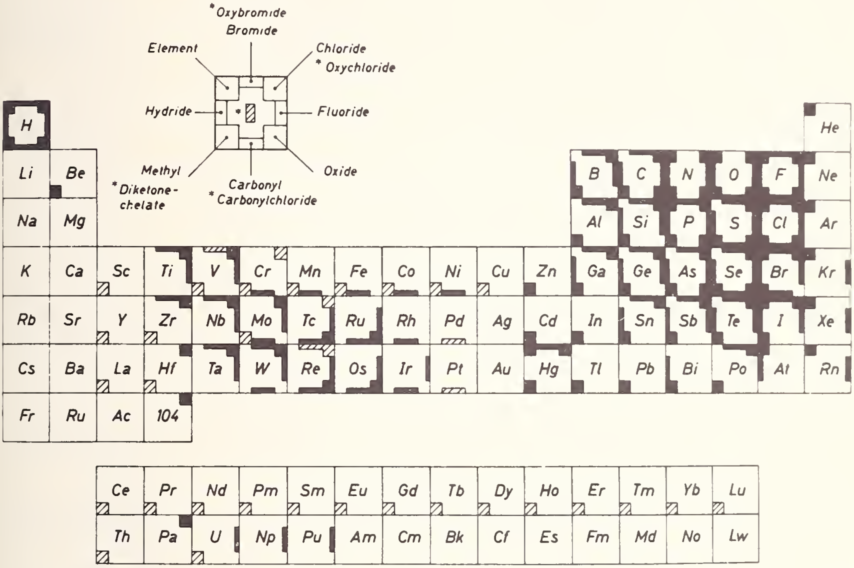

Figure 15. Volatile compounds with boiling or sublimation points below 350 °C. Solid or shaded areas indicate compounds with boiling or sublimation points below this limit. Solid areas refer to compounds indicated without asterisks in the insert, upper left. If these compounds are not volatile or not known, shaded areas are used to refer to compounds with asterisk in the insert. (Reprinted with permission of Herrmann [81].)

Procedures for the fluorination of metal ions are already available from gas chromatography, and they are claimed to be simple, rapid, and safe [82]. Should direct volatilization give rise to practical procedures, one could attempt to do separations directly in the gaseous phase.

Gas chromatography of metal ions is an applicable technique, which could couple very well with direct volatilization. Reactions between the gaseous phase and suitable inorganic compounds could be another possibility, which is worth exploring [83,84].

The main advantage of radiochemical separations in the gaseous phase would be that the separation could be rather rapid and require a minimum of work. It would also be rather satisfactory from the point of view of radiation hazard since the handling of the active specimen would be minimal and by keeping the pressure in the equipment below atmospheric the danger of contamination could be minimized.

VIII. References

[1] Heydorn, K., Trans. Amer. Nucl. Soc. **9,** 86 (1966).

[2] Heydorn, K., Trans. Amer. Nucl. Soc. **9,** 70 (1966).

[3] Ruzicka, J., Stary, J., "Substoichiometry in Radiochemical Analysis", Pergamon Press, Oxford (1968).

[4] Adaniek, A., Obrusnik, J., Kukula, F., Krivanek, M., Nuclear Activation Techniques in the Life Sciences, p. 189, IAEA, Vienna, (1967).

[5] Konig, R. H., Meyn, E., J. Inorg. Nucl. Chem. **29,** 1519 (1967).

[6] Alimarin, I. P., Perezhogin, F. A., Talanta **14,** 109 (1967).

[7] Ruzicka, J., Lamm, C. G., Talanta **15,** 689 (1968).

[8] Kolthoff, I. M., Elving, P. J., Treatise an Analytical Chemistry, Part I, Vol. 2, Interscience Publication, New York (1961).

[9] Mark, H. B., Berlandi, F. J., Anal. Chem. **36,** 2062 (1964).

[10] Schöninger, W., Mikrochim. Acta. 869 (1956).

[11] Van den Winkel, P., Speecke, A., Hoste, J. J., Nuclear Activation Techniques in the Life Sciences, p. 159, IAEA, Vienna (1967).

[12] Belisle, J., Green, C. D., Winter, L. D., Anal. Chem. **40,** 1006 (1968).

[13] Gleit, C. E., Holland, W. D., Anal. Chem. **34,** 1454 (1962).

[14] Neuburger, M., Fourcy, A., J. Radioanal. Chem. **1,** 289 (1968).

[15] Analytical Methods Committee: Analyst **85,** 643 (1960).

[16] Down, J. L., Gorsuch, T. T., Analyst **92,** 398 (1967).

[17] Analytical Methods Committee: Analyst **92,** 398 (1967).

[18] Bowen, H. J. M., Anal. Chem. **40,** 969 (1968).

[19] Bock Werthmann, W., Nuclear Activation Techniques in the Life Sciences, p. 173, IAEA, Vienna (1967).

[20] Morrison, G. H., Freiser, H., "Solvent Extraction in Analytical Chemistry", J. Wiley and Sons, New York (1962).

[21] Stary, J., "The Solvent Extraction of Metal Chelates", Pergamon Press (1964).

[22] Alian, A., Haggag, A., Talanta **14,** 1109 (1967).

[23] Baker, C. W., Brooke, N. M., Goode, G. C., Paper presented at the II S.A.C. Conference, Nottingham (1968).

[24] Cerrai, E., Chromatographic Reviews **6,** Elsevier Publ. Co., Amsterdam (1964).

[25] Samsahl, K., Aktiebolaget Atomenergi, Report AE-82 (1962).

[26] Samsahl, K., Anal. Chem. **39,** 1480 (1967).

[27] Travesi, A., Lee, Y. Y. Y., Nuclear Activation Techniques in the Life Sciences, p. 301, IAEA, Vienna (1967).

[28] Landstrom, O., Wenner, C. G., Report AE-204 (1965).

[29] Gebauhr, W., Radiochimica Acta, **4,** 191 (1965).

[30] Ross, W. J., Anal. Chem. **36,** 1114 (1964).

[31] Albert, P., Cuypers, M., Lesbats, A., Mignousin, E., in "Modern Trends in Activation Analysis", p. 310, College Station, Texas (1965).

[32] Op de Beeck, J., Hoste, J., Acta Chim. Acad. Sci. Hung. **53,** 137 (1967).

[33] Op de Beeck, J., Anal. Chim. Acta, **40,** 221 (1968).

[34] Buchtela, K., Aitzetmuller, K., Grass, F., J. Radioanal. Chem. **1,** 225 (1968).

[35] Girardi, F., Nuclear Activation Techniques in the Life Sciences, p. 117, IAEA, Vienna (1967).

[36] Qureshi, J. H., Nagi, F. I., J. Inorg. Nucl. Chem. **29,** 2879 (1967).

[37] Walton, H. F., Anal. Chem. **40,** 51 R (1968).

[38] Samuelson, O., Ion Exchange Separations in Analytical Chemistry, J. Wiley and Sons, New York (1963).

[39] Cummings, T., Korkisch, J., Talanta **14**, 1185 (1967).

[40] Korkisch, J., Feik, F., Ahluwalia, S. S., Talanta **14**, 1069 (1967).

[41] Korkisch, J., Ahluwalia, S. S., Talanta **14**, 155 (1967).

[42] Strelow, F. W. E., Anal. Chem. **40**, 928 (1968).

[43] Korkish, J., Orlandini, K. A., Chem. **40**, 1127 (1968).

[44] Auboin, G., Laverlochere, J., J. Radioanal. Chem. **1**, 123 (1968).

[45] Knoch, W., Muyn, B., Lahr, H., J. Chromatog. **20**, 122 (1965).

[46] Houtmann, J. P. W., Proc. Intern. Conf. on Activation Techniques in the Life Sciences, p. 171, IAEA, see discussion, Vienna (1967).

[47] Massart, D. L., Sainte, G., Hoste, J., Acta Chim. Acad. Sci. Hung. **52**, 229 (1967).

[48] Bark, L. S., Duncan, G., Graham, R. J. T., Analyst **92**, 347 (1967).

[49] Bark, L. S., Duncan, G., Graham, R. J. T., Analyst **92**, p. 31 (1967).

[50] Cram, S. P., Brownlee, J. L., J. Gas Chromatog. **6**, 305 (1968).

[51] Cram, S. P., Brownlee, J. L., J. Gas Chromatog. **6**, 313 (1968).

[52] Moshier, R. W., Sievers, R. E., Gas Chromatography of Metal Chelates, Pergamon Press (1965).

[53] IAEA Bibliographic Series No. 25, "Recovery of Fission Products", Vienna (1967).

[54] Bigliocca, C., Girardi, F., Pauly, J., Sabbioni, E., Meloni, S., Provasoli, A., Anal. Chem. **39**, 1634 (1967).

[55] Girardi, F., Guzzi, G., Pauly, J., Pietra, R., Proc. 2nd Intern. Conf. Modern Trends in Activation Analysis, p. 341, Texas A & M University (1965).

[56] Girardi, F., Sabbioni, E., J. Radioanal. Chem. **1**, 169 (1968).

[57] Nuclear Science Series "The Radiochemistry of the Elements", U.S.A. National Academy of Science.

[58] Bowen, H. J. M., Gibbons, D., Radioactivation Analysis, Claredon Press, Oxford (1963).

[59] Girardi, F., Guzzi, G., Pauly, J., Euratom Tech. Rept. EUR 1898.e (1965).

[60] Kyrs, M., Kadlecova, L., J. Radioanal. Chem. **1**, 103 (1968).

[61] Kim, C. K., Meinke, W. W., Proc. 2nd Int. Conf. Modern Trends in Activation Analysis, p. 316, Texas A & M University (1965).

[62] Wahl, W. H., Molinski, V. J., Arino, H., Modern Trends in Activation Analysis, Paper ICAA II/u, College Station, Texas (1965).

[63] Hogdahl, O. T., Melsom, S., Bowen, V. T., Advances in Chemistry Series **73**, 308 (1968).

[64] Cobb, J. C., Anal. Chem. **39**, 127 (1967).

[65] Girardi, F., Pauly, J., Sabbioni, E., Vos, G., Nuclear Activation Techniques in the Life Sciences, IAEA, Amsterdam (1967), Paper SM-91/10.

[66] Girardi, F., Merlini, M., "L'analyse par radioactivation et ses applications aux sciences biologiques, p. 23, Presses Universitaries de France, Paris (1964).

[67] Smales, A. A., Mapper, D., ibid, p. 157.

[68] Auboin, G., Diebolt, J., Junod, E., Laverlochere, J., Proc. 2nd Int. Conf. Modern Trends in Activation Analysis, p. 344, Texas A & M University (1965).

[69] Bock Werthmann, W., Schulze, W., ibid, p. 120.

[70] Ross, W. J., Anal. Chem. **36**, 1114 (1964).

[71] Pronin, V. A., Gilbert, E. N., Artyakhin, P. I., Izv. Sibirsk. Otd. Akad. Nank, SSSR, Ser. Khim. Nauk, **3**, 88 (1966).

[72] Gebauhr, W., Radiochim. Acta **4**, 191 (1965).

[73] Pinte, G., Report CEA-R 3267 (1967).

[74] Jervis, R. E., Wong, K. Y., Nuclear Activation Techniques in the Life Sciences, p. 137, IAEA, Vienna 1967.

[75] Samsahl, K., Wester, P. O., Landstrom, O., Anal. Chem. **40**, 181 (1968).

[76] Houtman, J. P. W., private communication.
[77] Samsahl, K., Analyst **93,** 101 (1968).
[78] Girardi, F., Merlini, M., Pauly, J., Pietra, R., "Radiochemical Methods of Analysis", **2, 3,** IAEA Vienna (1965).
[79] Comar, D., Le Poec, C., Proc. 2nd Intern. Conf. Modern Trends in Activation Analysis, p. 351, Texas A & M University (1965).
[80] Smales, A. A., in Trace Characterization, Chemical and Physical, p. 324, NBS Monograph 100 (1967).
[81] Herrmann, G., Arkiv. for Fysik **36,** 111 (1967).
[82] Zado, F. M., Juvet, R. S., Gas Chromatography 1966, p. 283-295.
[83] Wilson, J. R., Wilard, J. E., J. Phys. Chem. **70,** 1665 (1966).
[84] Chem. Tech. Div. Progress Report 1964, ORNL-**36,** 27 (1964).

CHAPTER 7

RADIOCHEMICAL SEPARATIONS

Synopsis of Discussions

PHILIPPE ALBERT, *Chairman*

Centre d'Etudes de Chimie
Metallurgique du C.N.R.S.
Vitry-sur-Seine, France

In actual fact, our session began with the Plenary Lecture by Dr. F. Girardi. His communication in our session gave him the possibility of presenting much more information on the results that he has obtained with the inorganic absorbers, hydrated antimony pentoxide (HAP), acid aluminum oxide, manganese dioxide (MnO_2), stannic oxide, cupric sulphide, cuprous chloride, and with the ions exchange resins: Dowex 1 and 50. The author has shown the very interesting possibility of combining Ge(Li) gamma-ray spectrometry with the selective chemical separation of the isotopes which give a high level of "Compton plateau". Successive "group chemical" separations can be selected by analysis of gamma-ray spectra. It is possible to reduce these to the minimum number and to detect very low levels of activities. Girardi called this technique "chemical spectrum stripping". I am sure it will be a very useful technique in the near future. Finally, this author proposed the use of computer calculations to make a scheme of chemical separations from a library of the behavior of the elements which is stored in the computer.

Beside this very systematic (but highly speculative) exploratory work we have had two other presentations on the subject of "group chemical" separations. S. F. Peterson, A. Travesi and G. H. Morrison have described experimental work on the analysis of 29 elements (39 radioisotopes) in rocks. This is made by chemical separation with HAP (Sb_2O_5), Dowex 1×8, TBP extraction in five groups only, and gamma-ray spectroscopy using Ge(Li) detectors. Except for Na, K, and Fe all the elements are at the part per million (ppm) level.

Barbara A. Thompson has described the group separations which were studied for the analysis of high purity zinc (ppb level) and for minor constituents in steel and cast iron. The Ge(Li) gamma-ray spectroscopy in these two examples gives the possibility of reducing the number of the chemical groups. A very good introduction is made in this paper of the guideline to be used for choosing a group separation procedure. Experimental results are given.

S. P. Cram and F. T. Varcoe presented the gas chromatographic separation of several transition metals which were separated as volatile metal chelates (chromium and copper). Several gas phase counting systems were described which were used for the pulse-height analysis of the chromatographic effluents. The combination of gas chromatography and neutron activation analysis was used for organic functional group analysis, the determination of molecular structure, and elemental analysis.

S. May and G. Pinte have given an extensive study on the radioactivation analysis of nuclear graphite. This work shows new and old results on the purity and purification of the graphite. Proposed separations are classical (precipitations, extractions by organic solvents, and ion exchange). Many tables describe the high purity of analyzed graphites and the very high sensitivity of the method.

S. Meloni, A. Brandone and V. Maxia, have described a very beautiful method of analysis for chromium in biological materials. Rapidity and simplicity are the main characteristics. The procedure uses an HAP fixation for sodium, SnO_2 for phosphorus, and finally chromium is counted on MnO_2.

I. H. Qureshi, L. T. McClendon, P. D. LaFleur, have studied the extraction coefficients of many elements into HDEHP (bis-2-ethylhexyl-orthophosphoric acid). They give numerous results in three tables.

Ch. Cleyrergue, N. Deschamps and Ph. Albert gave the variation of the partition coefficient, K_D, between the resin, Dowex 1×8, and the mixtures water-hydrochloric acid-acetone as a function of the concentration in acetone for 8 elements of periodic-table groups IB, VB, VIA and VIB. The results show a new behavior of these elements in many cases. New separations will result. It should be noticed that tungsten, antimony and gold can be more easily kept in solution than in water-acid media.

In the discussions of the papers, three main areas have been pointed out: (1) The "carrier free" separations can give "unknown loss" of chemical yield, and some people think it is better to add a few micrograms of inactive carrier before the sample dissolution. (2) The collection and irradiation of biological samples require particular attention, and contamination is always possible. (3) Some remarks have been made on the "oldish nature" of certain chemical separations which were described. I think on this point, that if one chemical procedure is fast, easy and with good yield, it's "age" is not important.

In this session we have seen that many new methods can be used to make better and faster separations such as: retention on inorganic compounds and ion exchange in organic media. Many other combinations are possible, and for example, in our laboratory Mr. N. Deschamps and Mrs. J. Blouri are currently studying the separation of many elements by stationary chromatography on polytrifluoromonochloroethylene with HDEHP. This compound has been used in extraction work by Peppard, *et al* for the rare earths and the actinides and by I. H. Qureshi *et al* and by R. Denig, N. Trautmann (Symposium at Julich, October 4, 1966) for many other elements.

From the work of this session we can point out three main new trends:

1. Ge(Li) gamma-ray spectrometry gives the possibility for a *new look* in systematic analysis by "group separation". These groups will be defined by the characteristics of the gamma rays and the composition of the mixture of the radioisotopes, more than by the chemical properties. For example, it will be necessary to extract from solution all of the radioisotopes which are identified by high energy gamma-ray peaks which cause Compton scattering. New peaks become evident, and repetition of this operation can be called "chemical stripping".

Depending upon the sensitivity needed (ppm or ppb) for the elements to be determined (cross section), either it will be possible to use Ge(Li) to reduce the number of chemical separations, or it will be necessary to use large NaI(Tl) crystals with more radiochemical separation steps.

2. Retention on inorganic compunds (Sb_2O_5, MnO_2, *etc.*) and ion exchange in inorganic and organic media give new possibilities of group chemical separations.

3. Gas chromatographic separation of volatile metal chelates or other compounds seems very promising.

In conclusion, it seems to me that in the near future, the idea of "systematic analysis" which has been developed in 1955-1960 in only a few laboratories specializing in fundamental research will result in a large expansion in simple, partially automated and consequently cheaper activation analyses. At this time, the computer's given scheme is only a preliminary approach, because trace analysis involves computer systematics that do not take into account the matrix effects (*e.g.* the large difference in concentration of the element). Much more work needs to be done on this concept.

GAS CHROMATOGRAPHIC SEPARATIONS IN NEUTRON ACTIVATION ANALYSIS

Stuart P. Cram and Fredrick T. Varcoe

Department of Chemistry
University of Florida
Gainesville, Florida 32601

I. Introduction

The inherent sensitivity of neutron activation analysis at trace concentrations is dependent upon accurately measuring the activity of the radionuclide and the energy of its photopeak. Interferences in the pulse-height spectra of real and complex samples arise from irradiation of the matrix materials, unresolved photopeaks, and Compton scattering from high energy photons. Long-lived materials with large cross sections also significantly reduce the analytical sensitivity of short-lived isotopes by giving rise to high analyzer dead times unless these interferences are separated before pulse-height analysis.

Post-irradiation separations in neutron activation analysis should be selective, rapid, efficient, and give complete recovery of the separated fractions in a carrier-free form. Many excellent radiochemical procedures exist for the isolation of specific radionuclides [1], but they are generally time-consuming, require manual laboratory manipulation, and are limited in scope. The analysis of trace amounts of 62 different elements using post-irradiation distillation, precipitation, and extraction for separation of 49 of the elements into six groups for subsequent analysis has been described [2]. In addition to being time-consuming, the separated fractions are not carrier free and the pulse-height spectra are still very complex and lack the optimum analytical sensitivity. Tera and Morrison [3] have reported the use of ion exchange chromatography and isotopic exchange for the removal of matrix activities in order to effect multitrace element separations from large amounts of radioactive materials. These separations are rapid and widely applicable for a large number of elements, but still require carriers and manual operation.

Gas-solid chromatography was used to separate krypton and xenon fission gas fractions in 15 seconds, and pulse-height analysis was used to identify the isotopes of each element present and to follow their decay [4]. Gas-liquid chromatography offers the greatest potential for the isolation of radionuclides in a carrier-free form as it is selective enough to permit counting of single radionuclides, has very high column efficiencies, and is fast enough to allow measurement of isotopes with half lives as short as 11 seconds [5,6]. The method is applicable to both organic and inorganic materials as more than three quarters of all of the elements in the periodic table have been separated by gas chromatography [7]. Group separations may also be considered if the sensitivity and spectral resolution are adequate for the required analysis.

II. Experimental

The experiments reported in this work are limited to post-irradiation separations as this represents the most generally applicable case and eliminates pretreatment of the sample before irradiation.

Following the reactor irradiation, liquid samples were injected into the gas chromatograph by an automated injection system, or with a solid sampler for the samples sealed in pyrex capillaries. High speed separations were used to separate the organic halides on columns with chlorofluorocarbon stationary phases. The high volatility of the low molecular weight hydrocarbons gave excellent resolution of the pulse-height spectra of the halogens, although the spectra had to be measured using the "parent peak" of the compound of interest as these samples showed the effects of Szilard-Chalmers reactions during irradiation. Consequently, degradation of the organic halides decreases the sensitivity and the absolute amount of material available for analysis. Nonpolar columns such as DC 710 silicone oil were used to separate the metal hexafluoroacetylacetonate complexes of several transition metals. Both isothermal and programmed temperature separations have been used due to the wide difference in boiling points, especially in the case of the metal complexes. The temperatures of the injection port and the partition column were found to be critical and were optimized in order to prevent thermal decomposition, adsorption, and condensation.

The chromatographic column effluents were analyzed by multichannel scaling and/or pulse-height scintillation spectrometry. Two 3 in. × 3 in. NaI(Tl) scintillation crystals were placed at the outlet of the chromatograph and connected to a 400 channel pulse-height analyzer. The resolution of the radiochromatogram was controlled by choosing the delay time of the counting period after injection and the counting time per channel. The activity of the sample and the retention time of the chromatographic bands, determined the counting method used to obtain the pulse-height spectrum.

III. Results and Discussion

In order to measure the pulse-height spectra for qualitative and quantitative analysis, several counting methods were evaluated. The flow-through technique requires a relatively high effluent activity, and the flow rate of purge carrier gas must be adjusted to maintain the resolution between the chromatographic peaks. This determines the counting time and necessarily limits the sensitivity. A series of concentric coils in the plane of the scintillation crystal proved to be preferable to a large volume, circular chamber geometry as the latter requires exponential dilution of the sample, although the former has the disadvantage of a continuously changing counting efficiency as a function of time.

Discontinuous methods of counting include the stop flow technique, which increases the total separation and analysis time, and is limited by diffusion of the chromatographic effluent on the column and in the active counting volume. Adsorption on small charcoal traps at liquid nitrogen temperatures is effective for counting trace amounts as the counting time may be extended indefinitely to reduce the statistical errors. Either the number of charcoal traps must equal the number of activated effluents or cumulative pulse-height spectra may be measured sequentially and later reduced by spectrum stripping.

The calculated limits of detection have been obtained by coupling gas-liquid chromatography with neutron activation analysis. This requires that the counting time be commensurate with the half life, and thus collection of the column effluents should be used for long-lived isotopes. Flow-through analyses were used for short-lived isotopes where the chromatographic resolution is sufficient to permit counting for three to four half lives.

The sensitivity of the analysis will be limited by the size of the sample which may be injected onto the column, but by considering the speed of separation required, column resolution, and sample size, any two of these may be optimized at the expense of the third. Therefore, milligram samples of the inorganic transition metal chelates were separated by sacrificing separation speed and by increasing the percent liquid loading on the column. These separations were still completed in less than 10 minutes.

The coupling of gas-liquid chromatography with neutron activation analysis will be shown to be effective for isolating trace quantities of radionuclides so that they may be analyzed in the absence of any pulse-height spectral interferences or masking activities. These high efficiency separations will give analytical results by single channel analysis as well as multichannel analysis for the case of complete chromatographic resolution. This coupling experiment is equally applicable to group separations and is being developed for both organic and inorganic analyses.

IV. References

[1] U.S. Atomic Energy Comm. Rept., Nucl. Sci. Series, NAS-NS.
[2] Ross, W. J., Anal. Chem. **36**, 1114 (1964).
[3] Tera, F., and Morrison, G. H., Anal. Chem. **38**, 959 (1966).
[4] Wahlgren, M. A., and Meinke, W. W., J. Inorg. Nucl. Chem. **24**, 1527 (1962).
[5] Cram, S. P., and Brownlee, J. L., J. Gas Chromatog. **6**, 305 (1968).
[6] Cram, S. P., and Brownlee, J. L., J. Gas Chromatog. **6**, 313 (1968).
[7] Sievers, R. E., Fourth International Symposium Advances in Gas Chromatography, New York, April 3-6, 1967.

RAPID GROUP SEPARATION METHOD FOR NEUTRON ACTIVATION ANALYSIS OF GEOLOGICAL MATERIALS[1]

S. F. Peterson,[2] A. Travesi[3] and G. H. Morrison

Department of Chemistry
Cornell University
Ithaca, New York 14850

High resolution lithium drifted germanium Ge(Li) gamma-ray detectors have been applied to the nondestructive activation analysis of geological materials. Cobb [1] determined abundances of several rare earth elements in a variety of rock types, and Gordon, *et al* [2] determined 23 elements in igneous rocks.

However, the complexities of the gamma-ray spectra from multi-element samples such as rocks often prevent the determination of many elements by strictly instrumental methods. The high activities produced from abundant, high cross section isotopes such as Mn, La, and Na often mask lower level activities from other short and medium half life elements, while the activities from such elements as Sc and Co interfere with long half-life measurements. For this reason, chemical group separations were developed to permit the full utilization of the desirable features of high resolution semiconductor detectors without the extra difficulty of separating individual elements. Exploited to its full potential, a large improvement in sensitivity, precision, time of analysis, and number of elements seen should be noted from the group separation procedure as compared to nondestructive activation analysis. While this work was in process, Tomura, *et al* [3] reported the determination of rare earth elements in rock samples after a chemical group separation.

The group separation procedure developed, separates the sample into five groups. Total time required for dissolving and separating four rock samples is about three to four hours. The steps employed require little personal attention, thus minimizing operator exposure to radiation from the sample and simplifying automation if desired.

U.S. Geological Survey standard rock, W-1, was used as a concentration standard, all other rocks being compared to W-1. It was felt

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[1] Research supported by Advanced Research Projects Agency.

[2] Present Address: Savannah River Laboratory, E. I. DuPont De Nemours and Company, Aiken, South Carolina 29801.

[3] National Aeronautics and Space Administration/European Space Research Fellow. Permanent Address: Junta de Energia Nuclear, Nuclear Chemistry Division, Madrid, Spain.

that using a complex sample such as W-1 as a standard would be more meaningful than using individual element standards. W-1 has been analyzed in many laboratories by several techniques, and values for most elements are fairly well established [4,5]. Also, the complexity of W-1 is similar to the material being analyzed.

II. Experimental

A. Reagents and Apparatus

Hydrated antimony pentoxide (HAP) was prepared by the slow addition of antimony pentachloride to distilled water. The precipitate formed was washed with distilled water and dried, first to a paste-like consistency at 110 °C and then for 7 hours at 270 °C. The dried crystals of HAP were ground in a mortar and pestle and sieved, the 40-80 mesh fraction being used.

Dowex 1X8, 200-400 mesh ion-exchange resin was washed with distilled water to remove the fines and equilibrated with 8 *N* HCl before use.

Samples were irradiated for 8 hours at a flux of 7×10^{11} $n \cdot cm^{-2} \cdot sec^{-1}$ in the rotary specimen rack of Cornell University's Triga Mark II reactor. Samples were allowed to cool for 15 hours, then chemically processed.

Counting was done using a 30 cm^3 coaxial Ge(Li) detector (Nuclear Diodes) and an RIDL 34-12, 400 channel pulse-height analyzer. System resolution is better than 3 keV full width half maximum (FWHM) at 1.33 MeV, with a peak to Compton ratio of better than 15:1. All group fractions were counted in 125 ml glass-stopped Erlenmeyer flasks containing 20 ml of solution. In order to obtain the desired resolution with the 400 channel analyzer, samples were counted in two energy regions using a biased amplifier: 0-0.9 MeV and 0.8-1.7 MeV.

Data analysis was performed by computer, utilizing the punch paper tape output from the analyzer. The programs used plot the spectra and determine background corrected peak areas.

B. Separation

The separation scheme is summarized graphically in Figure 1. Approximately 1 g samples of U.S. Geological Survey standard rocks W-1, G-2, BCR-1, PCC-1, AGV-1, GSP-1 and DTS-1 were used in the study. Before dissolving, 1-2 mg carriers of Sc, Zn, and La were added. The sample was then dissolved in a platinum crucible with 2-3 ml of concentrated H_2SO_4 and 10-15 ml of 48% HF with gentle heating on a hot plate. The heating was carried out to the appearance of SO_3 fumes, and more HF added. This was repeated several times until the sample was

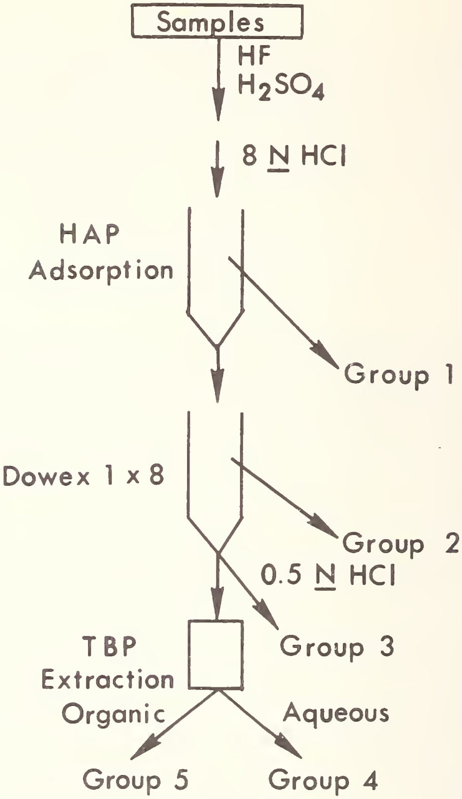

Figure 1. Schematic of chemical group separation method for neutron activation analysis of geological materials.

completely dissolved, then the sample heated to dryness. The SiF_4 formed was allowed to escape. Negligible gamma-ray activity was measured in the material collected in a trap over the sample.

The residue was dissolved in 20-25 ml of 8 *N* HCl and batch extracted for 10 minutes with 3 g of HAP [6]. The material was then passed through a small (1 cm diameter by 2.5 cm high) column of HAP and washed with 50 ml of 8 *N* HCl at a flow rate of 2-3 ml/min until the effluent was colorless. The washed HAP was transferred to a container for counting after suitable decay of ^{24}Na.

The effluent of the HAP column was passed through a 1 cm by 10 cm column of Dowex 1X8, 200-400 mesh ion-exchange resin at a flow rate of 1-2 ml/min and washed with 50 ml of 8 *N* HCl at the same flow rate.

The effluent and wash were evaporated to near dryness and taken up in 20 ml of 8 *N* HCl. This solution was extracted twice with first 20 ml and then 10 ml of HCl pre-equilibrated tri-n-butyl phosphate (TBP).

The anion exchange column was eluted with 25 ml of 0.5 *N* HCl, and the eluate added to a 125-ml Erlenmeyer flask for counting. The resin was similarly added to a counting container.

III. Results and Discussion

Table 1 lists the chemical groups with the radioisotopes appearing in each group. Also listed are the half life of the isotopes, their chemical yields, major photopeak energies with observed relative peak areas (largest peak for an element = 100), and notes on possible interferences. Information is presented for 29 elements (39 isotopes). The chemical yield is the percent of that element's activity appearing in the separation group. The yield was studied using tracers and calculated from the distribution of the radioisotopes in the groups.

Table 2 gives results for 16 elements determined in U.S. Geological Survey standard rocks G-2, BCR-1, and PCC-1. The calculations were made using W-1 as a standard. Values for elements in W-1 as given by Gordon [2] and others [5, 7] are listed, along with the concentration taken as the standard value in this work.

As a cross check on W-1 concentrations, several of the higher activity elements were determined nondestructively and compared to values found by the separation procedure. This determined the overall yield of the separation method. It was found that essentially all the activity from a sample ends up in the 5 groups with negligible loss during separation. The general agreement of calculated and literature values for G-2, BCR-1 and PCC-1 further confirms the suitability of using W-1 as a standard in the analysis of other, even dissimilar rocks.

No attempt has been made to determine sensitivity or detection limits. These values are readily available from many sources, both from a theoretical standpoint [8] and actually observed [9]. Actual values of sensitivity for complex samples such as rocks will be seen to vary considerably, depending on interferences and activities from other elements in the same group, general background levels, etc.

Precision values were not assigned to the data in Table 2. In general, the concentration values determined are ± 10% to ± 20%, depending on activity in the photopeak, counting time, interferences, and general background levels.

Table 1. Chemical groups and properties of nuclides observed.

Radioisotope	Half life	Chemical yield (%)	Energy (MeV)	Relative area	Notes and interferences
		Group 1: Hydrated antimony pentoxide adsorption			
^{24}Na	15 h	99.9	0.346	20	escape peak
			0.511	--	anihilation
			1.368	100	
			1.73	25	escape peak
^{182}Ta	115 d	100	0.100	100	
			0.15	52	
			0.179	18	
			0.222	25	
		Group 2: Ion–exchange, resin			
^{65}Zn	245 d	100	0.511	1	
			1.114	100	1.112 ^{46}Sc[a]
^{69m}Zn	13.8 h	100	0.438	100	
^{115}Cd	54 h	N.C.[b]	0.335	100	
			0.523	25	
^{115m}Cd	43 d	N.C.	0.485	--	
			0.935	100	
			1.295	--	
^{122}Sb	2.8 d	100	0.564	100	0.559 ^{76}As[a]
			0.687	4	
^{124}Sb	60 d	100	0.603	100	
			0.722	10	
^{186}Re	3.7 d	100	0.137	100	
			0.631	--	
^{188}Re	17 h	100	0.155	100	
			0.478	--	
			0.820	--	
^{192}Ir	74.4 d	N.C.	0.295	40	
			0.317	100	
			0.468	33	
^{194}Ir	19 h	N.C.	0.328	100	
			0.645	4	
			0.932	2	
^{198}Au	64.8 h	100	0.411	100	
			0.676	1	

Table 1. Chemical groups and properties of nuclides observed. (continued)

Radioisotope	Half life	Chemical yield (%)	Energy (MeV)	Relative area	Notes and interferences
Group 3: Ion–exchange, eluate					
^{59}Fe	45 d	99.9	0.143	17	
			0.192	44	
			1.095	100	1.085 ^{116m}In
			1.292	64	1.293 ^{116m}In
^{60}Co	5.3 y	100	1.173	100	
			1.332	83	
^{64}Cu	12.8 h	98	0.511	100	
			1.34	1	1.332 ^{60}Co
^{65}Ni	2.56 h	100	0.368	100	
			1.114	60	
			1.48	50	
^{72}Ga	14.1 h	95	0.635	34	
			0.832	100	0.835 ^{56}Mn
^{76}As	26.5 h	99	0.559	100	0.552 ^{187}W
			0.657	9	
			1.22	4	
^{116m}In	54 min	96	0.417	100	seldom observed
			1.085	50	1.095 ^{59}Fe
			1.293	50	1.292 ^{59}Fe
^{187}W	24 h	N.C.	0.134	100	
			0.480	50	
			0.686	41	
Group 4: Extraction, aqueous phase					
^{51}Cr	27 d	99	0.320	100	0.328 ^{194}Ir[a]
^{140}La	40.2 h	95	0.328	60	
			0.487	100	
			1.595	55	
^{141}Ce	33.1 d	98	0.145	100	0.143 ^{153}Sm
^{152m}Eu	9.3 h	98	0.122	100	
			0.344	20	
			0.963	20	

Table 1. Chemical groups and properties of nuclides observed.
Group 4: Extraction, aqueous phase (continued).

Radioisotope	Half life	Chemical yield (%)	Energy (MeV)	Relative area	Notes and interferences
^{152}Eu	12 y	98	0.122	--	
			0.344	--	
			0.779	--	
^{153}Sm	47 h	98	0.07	--	
			0.103	100	0.103 ^{153}Gd
			0.143	5	
^{153}Gd	236 d	98	0.103	100	0.103 ^{153}Sm
^{159}Gd	18 h	98	0.225	5	
			0.362	100	
^{160}Tb	73 d	98	0.197	40	
			0.298	100	
			0.966	20	0.963 ^{152m}Eu
^{169}Yb	32 d	98	0.118	100	
			0.13	100	
			0.198	50	
^{175}Yb	4.2 d	98	0.114	100	^{169}Yb, ^{177}Lu
			0.283	30	
			0.396	45	
^{177}Lu	6.8 d	98	0.113	100	^{175}Yb
			0.208		
Group 5: Extraction, organic phase.					
^{46}Sc	84 d	95	0.889	100	
			1.120	65	
^{56}Mn	2.6 h	N.C.	0.847	100	
			1.81	10	
^{95}Zr	65 d	N.C.	0.725	100	
			0.757	90	
^{97}Zr	17 h	N.C.	0.666	100	
			0.75	80	
^{175}Hf	70 d	N.C.	0.089	10	
			0.343	100	0.348 ^{181}Hf

Table 1. Chemical groups and properties of nuclides observed.
Group 5: Extraction, organic phase (continued).

Radioisotope	Half life	Chemical yield (%)	Energy (MeV)	Relative area	Notes and interferences
^{181}Hf	43 d	N.C.	0.130	100	
			0.348	5	
			0.482	30	

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[a] Interference from element in different chemical group.

[b] N.C. = not calculated.

Table 2. Concentration of elements observed in rock samples.[a]

Element	W–1	G–2	BCR–1	PCC–1
Sodium (%)				
This work	1.68[b]	2.80	1.70	0.04
Gordon[c]	1.68	2.95	2.40	– –
Others	1.53–1.54[d]	2.89–3.07[e]	2.33–2.46[e]	<.05[e]
Potassium (%)				
This work	.54	6.5	1.2	.14
Gordon	.8	4.0	1.2	– –
Others	.53– .57	4.0 –4.5	1.2 –1.3	<.05
Iron (%)				
This work	7.5	1.75	9.0	.14
Gordon	7.5	1.72	9.0	– –
Others	7.78	1.77	9.3 –10.7	– –
Cobalt				
This work	50	5.7	36.5	116
Gordon	46	4.3	36.3	– –
Others	40–53	3–6	26–40	90–120
Copper				
This work	110	14	17	11
Others	100–130	9–14	19–33	7–13
Gallium				
This work	16	27	21	N.D.[f]
Others	13–19	20–28	16–32	<10
Lanthanum				
This work	12	84	24	0.2
Gordon	12	81	23	– –
Others	11–30	82–130	22–40	<40
Zinc				
This work	82	92	118	17
Others	72–100	– –	– –	– –

Table 2. Concentration of elements observed in rock samples.[a] (continued)

Antimony				
This work	1	.06	.75	1.3
Gordon	1	<.06	1.1	––
Others	0.3 –1.2	.015–.10	.32– .69	––
Scandium				
This work	34	4.5	32	11
Gordon	34.8	3.5	32.5	––
Others	33–34	4–<7	29–53	8–10
Chromium				
This work	99	15	24	2150
Gordon	99	4.6	19	––
Others	98–125	6–12	9–27	1600–3600
Element	W–1	G–2	BCR–1	PCC–1
Europium				
This work	1.1	1.15	0.80	N.D.
Gordon	1.08	1.37	1.95	––
Others	1.0 –1.29	––	––	––
Cerium				
This work	21	140	35	N.D.
Gordon	21	144	46	––
Others	15–70	<400	<400	––
Lutetium				
This work	.44	.16	.70	N.D.
Gordon	.44	.18	.60	––
Others	0.20–5.0	––	––	––
Ytterbium				
This work	2.2	.85	3.1	N.D.
Gordon	2.2	.80	3.2	––
Others	2.1 –5.0	––	––	––
Terbium				
This work	.57	.40	.93	N.D.
Gordon	.57	.52	1.0	––
Others	.49– .80	––	––	––

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[a] ppm unless % indicated.

[b] W–1 concentrations taken as standard values in this work.

[c] Gordon, G. E., et al., Geochim. Cosmochim. Acta **32**, 369 (1968).

[d] Fleischer, M., Geochim. Cosmochim. Acta **29**, 1263 (1965).

[e] Flanagan, F. J., Geochim. Cosmochim. Acta **31**, 289 (1967).

[f] Not detected.

IV. References

[1] Cobb, J. C., Anal. Chem. **39,** 127 (1967).

[2] Gordon, G. E., Randle, K., Goles, G. G., Corliss, J. G., Beeson, M. H., and Oxley, S. S., Geochim. Cosmochim. Acta **32,** 369 (1968).

[3] Tomura, K., Higuchi, H., Miyaji, N., Onuma, N., and Hamaguchi, H., Anal. Chim. Acta **41,** 217 (1968).

[4] Fleischer, M., and Stevens, R. E., Geochim. Cosmochim. Acta **26,** 525 (1962).

[5] Fleischer, M., Ibid. **29,** 1263 (1965).

[6] Girardi, F., and Sabbioni, E., J. Radioanalyt. Chem. **1,** 169 (1968).

[7] Flanagan, F. J., Geochim. Cosmochim. Acta **31,** 289 (1967).

[8] Buchanan, J. D., In Trace Analysis, Physical Methods, G. H. Morrison, Ed., Interscience, New York, 1965, p. 345.

[9] Lyon, W. S., Guide to Activation Analysis, Van Nostrand, Princeton, 1964.

GROUP RADIOCHEMICAL SEPARATIONS: A PRACTICAL APPROACH TO ACTIVATION ANALYSIS

Barbara A. Thompson

Analytical Chemistry Division
National Bureau of Standards
Washington, D. C. 20234

I. Introduction

One of the primary objectives of the scientist conducting research in the field of activation analysis should be to advance the value of the method. To accomplish this objective he will direct his efforts toward making activation analysis so accurate, so precise, so sensitive, so rapid, and so universally applicable that everyone will want to use it. In this paper we shall consider the purpose and place of group separations in these efforts.

The use of group separations has increased sharply in the last few years (see, for example, References [1-4]). The obvious advantage to their use is the saving in time and thus, cost of analysis. An additional advantage, less obvious at first glance, is that by dividing the sample into groups, all of which are examined, it may be possible to observe the presence of elements which might not have been detected otherwise. The group separation approach does not usually yield improvements in precision, accuracy, or sensitivity over methods in which selected elements are individually separated chemically. In fact, one of the principal problems in developing a group separation procedure is to avoid paying a high price in reductions in precision, accuracy, and sensitivity for the saving in time. In the balance of this paper we shall discuss some guidelines for choosing a group separation procedure for a particular sample and also the application of these principles to the activation analysis of NBS Standard Reference Material (SRM) steels and high purity zinc.

II. Experimental

A. CHOICE OF TECHNIQUE

In approaching every new activation analysis problem one must ask two mandatory questions: First, what is the nature of the matrix and, second, what is the desired information. The choice of experimental technique depends entirely on the answers to these two questions. It is usually a mistake to expect to fit every sample to the same "black box" method. The next question to be asked is whether the desired information can be obtained by nondestructive analysis. Often the answer is negative; however, the advantages of nondestructive analysis are so great that it should certainly be employed in favorable situations.

In cases where chemical separations are required the following guidelines can be employed in selecting a particular procedure. First, the separations chosen should be rapid to obtain the maximum advantage of the group separation approach. The ion exchange methods of Samsahl [2,3] and Jervis and Wong [4] are excellent examples of the application of this principle. Not all matrices lend themselves to direct use of ion exchange, however, and the analyst should be prepared to utilize other types of chemistry such as solvent extraction or even precipitation in special situations. Second, it is important that the individual steps be quantitative so that time-consuming determinations of chemical yields are not necessary. Finally, the high resolution of Ge(Li) detectors should be utilized where appropriate, so that the sample is separated into the minimum number of groups. Each separated fraction must be counted and if more fractions than necessary are produced, the full time-saving potential of the group separation approach may not be realized.

B. EXAMPLES

In this laboratory we have applied these guidelines to the determination of several impurities at the part per billion (ppb) level in high purity zinc and to the determination of minor constituents in steel and cast iron. The sample size for the zinc analysis was about 1 g and that for the steels was 100 mg and so solvent extraction techniques were used in both cases. In addition, a preliminary silver chloride precipitation was carried out on the zinc samples.

The procedures chosen are shown schematically in Figures 1 and 2. The elements of interest in the steels were Cu, As, Cr, Co, W, and Mo. The only separations necessary for this group, if a Ge(Li) detector is used, are that of Mo away from the Fe matrix and of As away from any Sb which may be present. Thus, the samples were divided into the three fractions shown and all three were examined. The W, Mo fractions were counted with a 3 in. × 3 in. NaI(Tl) detector and the remaining two fractions were counted with a 30 cm^3 Ge(Li) detector.

Four fractions were separated from the zinc, but the remaining fraction containing the zinc could not be counted because of the high radioactivity of the various zinc isotopes and of copper isotopes produced by (n,p) reactions on the zinc matrix.

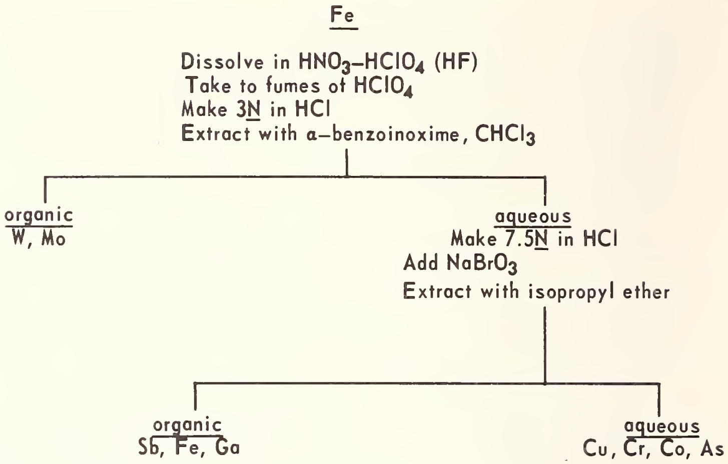
Fe
Dissolve in HNO_3–$HClO_4$ (HF)
Take to fumes of $HClO_4$
Make 3N in HCl
Extract with α–benzoinoxime, $CHCl_3$
organic
W, Mo
aqueous
Make 7.5N in HCl
Add $NaBrO_3$
Extract with isopropyl ether
organic
Sb, Fe, Ga
aqueous
Cu, Cr, Co, As

Figure 1. Group separations for steels.

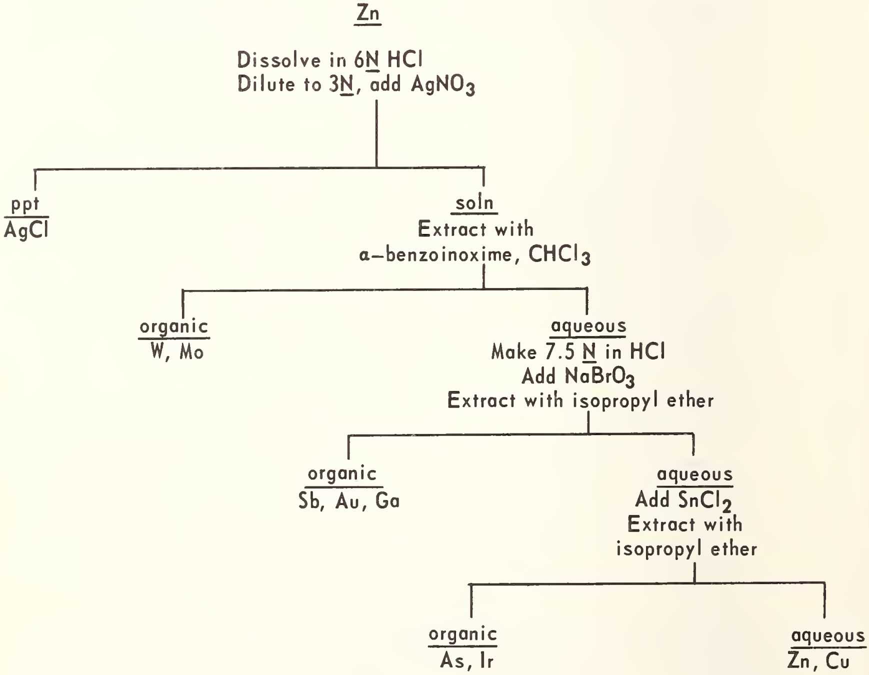

Figure 2. Group separations for zinc.

III. Results and Discussion

The results obtained for the steels are summarized in Table 1. NBS certified values are shown for comparison where available. It can be seen that precisions of ±10% at the 95% confidence level are routinely obtained, while in favorable situations the precision can be ±2%. The analysis is not limited to the elements listed in the table, which were the only ones observed to be present in the samples. Upper limits for the concentrations of Au, Zn, Sc, Na, and a number of other elements could have been calculated from the spectra of the fractions.

Table 1. Results of activation analysis of NBS steels, percent.

Steel	Cu	Co	As	Cr	W	Mo	Ga	Sb
101e								
A	0.359	0.18	–	17.98	0.056	0.426	–	–
B	0.355 ± 0.005[a]	0.18 ± 0.01	0.0077 ± 0.0002	ND[b]	0.046 ± 0.008	0.441 ± 0.04	0.0044 ± 0.0005	0.0005 ± 0.0005
101f	0.029 ± 0.001	0.090 ± 0.003	0.0028 ± 0.0002	ND	0.00026 ± 0.00003	0.0086 ± 0.0008	0.0040 ± 0.0003	0.0009 ± 0.0001
101g	0.029 ± 0.001	0.090 ± 0.002	0.0028 ± 0.0002	ND	0.00028 ± 0.00002	0.0029 ± 0.0004	0.00325 ± 0.00009	0.0013 ± 0.0001
6f								
A		–	0.032	0.442	–	0.009	–	–
B		0.002	0.032 ± 0.003	0.42 ± 0.02	0.0026 ± 0.0001	0.0091 ± 0.0007	ND	ND
14e								
A		–	–	0.072	–	0.013	–	–
B		0.002	ND	0.078 ± 0.004	0.00100 ± 0.00004	0.0114 ± 0.0004	ND	ND
73b								
A		–	–	12.81	–	0.014	–	–
B		0.006	ND	13.05 ± 0.25	0.0055 ± 0.0001	0.014 ± 0.001	ND	ND

---

[a] Limits quoted are $ts/\sqrt{n}$ for the 95% confidence level.

[b] ND = Not determined.

Note: A = NBS certified value.
B = Found in this work.

The results of the zinc analysis are shown in Table 2. Because of the high purity of the zinc, only upper limits could be determined for most of the elements reported. Those which were observed to be present, namely, Sb, Ag, and Au, appeared to be distributed inhomogeneously within the samples.

The group separations chosen in both cases were rapid; the total time of analysis for six replicate steel samples or four zinc samples was about two hours, not including sample dissolution. Tracer experiments showed the chemical yields to be greater than 99% in nearly every case. (Only 97% of

Table 2. Analytical results on zinc, ppb.

	Intermediate purity		High purity
	Pellets	Bar	
Silver	800–1200	1230–1360	--
Antimony	290– 530	17– 77	0.02 –2.1
Gold	< 0.1	1– 12	<0.002–0.02
Gallium	< 2	< 1	<0.1
Scandium	<10	< 3	< 3
Arsenic	< 0.3	< 2	< 0.2
Molybdenum	<20	<20	<10
Tungsten	< 0.04	< 0.07	< 0.04
Iridium	< 5	--	--

the W was extracted with α-benzoinoxime and only 97% of the As remained in the aqueous phase after the first ether extraction.) For the zinc samples decontamination factors of about 10^3 from Zn and Cu were obtained for the ether fractions and about 10^4-10^5 for the W, Mo fractions.

The Ge(Li) detector made it possible to determine a number of elements in the steels with good precision and accuracy by dividing the sample into a relatively small number of groups. Also, the use of a Ge(Li) detector allowed the same methods to be applied to a wide variety of compositions ranging from cast iron to high-chromium stainless steel. Only slight modifications were necessary to adapt the same separation scheme to the analysis of high purity zinc.

IV. References

[1] Girardi, F., in Nuclear Activation Techniques in the Life Sciences, IAEA, Vienna, 1967, pp. 117-135.

[2] Samsahl, K., Nukleonik **8,** 252 (1966).

[3] Samsahl, K., Analyst **93,** 101 (1968).

[4] Jervis, R. E., and Wong, K. Y., Nuclear Activation Techniques in the Life Sciences, IAEA, Vienna, 1967, pp. 137-158.

RADIOCHEMICAL SEPARATIONS BY RETENTION ON INORGANIC PRECIPITATES

F. Girardi, R. Pietra, and E. Sabbioni

Chemistry Department
C.C.R. EURATOM
Ispra, Varese, Italy

I. Introduction

Interest in the use of inorganic materials as column fillings in chromatographic separations for activation analysis arises from the high selectivity which can often be obtained by their use. Furthermore the behavior of most ions in a certain medium is different on different materials, thus providing a simple means to afford group separations by passage through a series of columns filled with proper materials. Automation of such a scheme would be rather simple.

After reporting a few applications [1-4] we decided to do an experimental survey of the behavior of ions in a variety of materials and from different media. Aim of this survey was: (1) to search for simpler ways of making radiochemical separations of interest for our work; (2) to see whether correlation on the behavior of different materials was possible which would help both in trying to explain different reaction mechanisms and to choose new materials; (3) to provide starting data for an attempt on "computer aided radiochemistry".

The survey was done in the following conditions: adsorption of the ion: 2 ml; washing volume (same acid molarity): 28 ml; column dimensions: 7 mm diam × 30 mm length. Flow rate = 1-1.5 ml/min (by gravity). The runs were done at room temperature. Table 1 summarizes the material/medium couples studied until the end of June, 1968. The results of each run were schematically reported by classifying the behavior of the element into one of three groups: (a) element completely retained; (b) element completely eluted; (c) element partially retained. No attempt was done to optimize the experimental conditions for each element until it was adsorbed or eluted completely. Data were collected on two kinds of tabulations: (a) behavior of different elements for each couple, column/medium, (periodical table); (b) behavior of different couples column/medium, for each element. The tables were periodically prepared by a properly developed computer program as long as the experiments proceeded.

Table 1. Couples material/medium studied at the end of June 1968.[a]

Acids	Hydrochloric			Nitric				Hydrofluoric	Perchloric		Sulphuric		Potential usefulness
	1M	6M	12M	0.1M	1M	7M	14M	6M	1M	6M	1M	3M	
Hydrated manganese dioxide (HMD)	–	–	–	61	50	–	51	52	52	–	–	–	yes
Anhydrous manganese dioxide	–	–	–	–	–	–	51	51	52	–	–	–	yes
Silicon dioxide	–	–	–	–	–	49	–	–	49	–	–	–	no
Acid alumina	–	–	–	–	–	49	–	–	49	–	–	–	yes
Hydrated antimony pentoxide (HAP)	–	58	60	–	36	34	53	54	51	36	–	–	yes
Antimony tetroxide	–	–	36	–	36	36	36	36	–	36	–	–	little
Antimony trioxide	–	–	–	–	21	21	22	20	–	–	–	–	no
Cadmium oxide	–	–	–	59	–	–	–	–	–	–	–	–	yes
Tin dioxide	57	–	–	41	60	58	50	50	51	–	–	–	yes
Zirconium phosphate	–	39	–	–	–	41	–	–	–	38	35		yes
Tin phosphate	–	–	–	–	–	34	–	–	–	33	34		little
Acid titanium phosphate	–	39	–	–	–	42	–	–	–	39	41		yes
Copper sulphide	–	34	–	–	–	34	–	–	–	34	33		yes
Cadmium sulphide	–	–	–	–	–	–	–	35	–	–	–		no
Cuprous chloride	–	–	–	–	–	–	–	37	–	37	35		yes
Lead fluoride	–	–	–	–	–	–	–	32	–	–	32		no
Cerium oxalate	–	–	–	–	–	–	–	39	–	–	37		
Dowex 1 × 8	–	33	–	–	–	32	–	33	–	33	–		yes
Dowex 50 × 8	–	32	–	–	–	32	–	33	–	33	–		little

[a] Figures are number of ions whose behaviour was measured for that couple.

Since work is still under way it is difficult to present the results in a summarized form. Therefore, only a few topics are summarized.

1. Out of seventeen materials presently studied, six did not present a special interest. Among the nine oxides examined HMD, HAP, SnO_2 give a variety of useful applications. The retention of radiosodium on HAP was studied in media other than in HCl as described in reference [2]. Although the selectivity was lower, useful applications can still be found in the biological field.

2. The remarkable well known affinity of Al_2O_3 for phosphates is coupled to a sufficiently high selectivity to make this material interesting for the reduction of bremsstrahlung from gamma spectra of biological specimens.

3. The three phosphates of Zr, Ti, and Sn (commercial inorganic exchangers) still keep good exchange properties at high ionic strength.

4. Copper sulphide can be used successfully for separating copper by isotopic exchange, while cuprous chloride has a marked affinity for bromides and iodides and it could perhaps be useful to remove ^{82}Br which frequently interferes in analyses.

5. Cation and anion exchange resins have also been examined in the same way, mainly for comparison of properties. This comparison showed that the action of each inorganic material is remarkably different from these "referees".

II. Development of Schemes and Automation

It appears from the data collected up to now that a variety of schemes could be prepared to solve different problems. The behavior of various materials in the same medium is different enough to permit many group separations by simple superimposition of columns. It also appears that "chemical spectrum stripping" should be possible with a proper choice of materials.

Automation of these chemical separations would be possible by means of simple machines, in which most parts in contact with radioisotopes can be disposed, thus simplifying decontamination problems and passage from one kind of separation to another.

III. Computer Coupled Radiochemistry

The particular kind of classification of behavior of the chosen elements lends itself to an easy construction of radiochemical separations by simple addition of properly chosen steps (or couples column/medium). The information can in fact be assembled in a three-dimensional matrix (parameters: element, column, medium) in which, by means of Boolean algebra, the different solutions for a given problem can be investigated.

This can be obtained in a simplified form by superimposition of cards in which the behavior of elements is represented by punched holes (a technique frequently used for storage and retrieval of bibliographic references) or in a more complete form by computer processing.

IV. References

[1] Girardi, F., Guzzi, G., Pauly, J., Pietra, R., Proc. II Intern. Conf. Modern Trends in Activation Analysis, Texas A&M University, 1966.

[2] Bigliocca, C., Girardi, F., Pauly, J., Sabbioni, E., Meloni, S., Provasoli, A., Anal. Chem. **39,** 1634 (1968).

[3] Girardi, F., in "Activation Techniques in the Life Sciences, p. 117, IAEA, Vienna. 1967.

[4] Girardi, F., Sabbioni, E., J. Radioanal. Chem. **1,** 169 (1968).

CHROMIUM SEPARATION BY INORGANIC EXCHANGERS IN ACTIVATION ANALYSIS OF BIOLOGICAL MATERIALS

Sandro Meloni, Alberto Brandone and Vera Maxia

Laboratorio di Radiochimica
Istituto di Chimica Generale
Universita di Pavia
27100 Pavia, Italy

I. Introduction

Trace element analysis in biological material has recently received much interest in order to establish the role played by trace elements in physiological processes. Many authors have shown or suggested a relationship between the trace element content and the occurrence of some diseases [1-6]. Thereafter trace element determination needs reliable analytical methods capable to give precise and accurate results.

As trace element concentration in human body is in the range 10^{-6}-10^{-12}g/g tissue, neutron activation analysis seems to be the technique capable to yield reproducible and accurate data. Unfortunately, instrumental methods can rarely be applied because of the strong interference from mineral macro-components of the biological matrix. Tedious chemical separations are then often required which are time consuming and during which many errors may be introduced.

Neutron activation analysis of chromium in biological materials has been proposed by several authors [4,6-10] and the separation techniques used involve distillation, solvent extraction, redox processes, ion exchange *etc*.

Recently in collaboration with the Nuclear Chemistry Group of CCR Euratom, Ispra (Italy), we investigated the selective sorption properties of some inorganic materials [11-15]. In this work the chemical separation of chromium was carried out using three inorganic adsorbers in cascade: hydrated antimony pentoxide (HAP), tin dioxide and manganese dioxide. This separation appears to be useful in the chromium determination by activation analysis of blood.

The reasons leading to the use of these adsorbers are the following: HAP allows the removal of sodium (^{24}Na) from the mineralized blood [15], tin dioxide adsorbs the phosphate ions thus getting rid of the ^{32}P which is responsible for the bremsstrahlung [14]. The latter would hamper the use of instrumental or partially instrumental techniques. Manganese dioxide strongly adsorbs chromium which may then be counted on this matrix [11]. What we suggest is a neutron activation method for chromium analysis based on carrier free chemical separations which are performed in a relatively short time.

II. Experimental

A. SAMPLE PREPARATION AND IRRADIATION

The biological material considered so far consisted of human blood serum and red cells. Aliquots of each, usually 0.5-1 ml, were pipetted in quartz vials and dried in an oven at 50-60 °C. The vials were then sealed and put in the irradiation container together with a chromium standard in the form of ammonium chromate solution. The irradiation was carried out for 30 hours in the rotatory specimen rack of the Triga Mark II LENA reactor of the University of Pavia where the thermal flux is $1.0 \times 10^{12} \text{n} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$.

B. CHEMICAL PROCEDURE

After a cooling time of about 2 days the quartz vials are broken and the blood mineralized with conc. nitric acid and hydrogen peroxide.

The nitric solution is heated to dryness under a infrared lamp and taken up to 10 ml with 1 M HNO_3. This solution is then poured onto a HAP column (7 mm diameter, 50 mm high). At this nitric acid molarity sodium and potassium, whose concentrations are 10^3 to 10^4 times higher than that of chromium [16], are strongly adsorbed on HAP [15]. The HAP column is then washed with 15-20 ml of 1 M HNO_3.

Chromium is not adsorbed on HAP and therefore goes into the eluate together with other elements. One of them, phosphorus, present as PO_4^{3-}, at the level of 0.28-0.48 mg/ml [16] is particularly troublesome because of the bremsstrahlung from the ^{32}P energetic beta rays. This radiation masks the low energy zone of the gamma spectrum where the ^{51}Cr 0.32 MeV gamma ray is located. To get rid of the phosphate anions the eluate is evaporated to about 10 ml and then passed through a SnO_2 column 8 mm in diameter, 60 mm high. The column is kept at 60 °C by a water jacket. The phosphate anions stick onto the column whereas chromium present as Cr(III) is eluted by washing with 15-20 ml of 1 M HNO_3. A few drops of conc. HNO_3 containing some potassium chlorate are added to the eluate in order to oxidize Cr(III) to Cr(VI). This step is necessary to ensure a complete sorption of chromium on manganese dioxide [11]. The solution is then passed through a MnO_2, column or, better, is shaken for about 1 hour with 400 mg of 100-200 mesh manganese dioxide in small bottles. The manganese dioxide is then separated from the solution by filtering on a large filter paper, which is in turn washed several times with 1 *M* nitric acid and distilled water. The filter is then dried in an oven at 110 °C and mounted on an aluminum card for counting.

Radioactivity measurements are carried out by gamma spectrometry using a 7.6 cm × 7.6 cm NaI(Tl) crystal connected to a 400 channel pulse-height analyzer. Manganese dioxide disk and chromium standard, which had been adsorbed on filter paper and mounted on an aluminum card, are counted under the same geometry.

III. Results and Discussion

A. RESULTS

By comparing the net 0.32 MeV photopeak areas of manganese dioxide disk and chromium standard spectra, the chromium content is readily obtained. The results are listed in Table 1. To check the validity of the proposed method we analyzed aliquots of the same blood with the technique described by van Kooten [10] involving carrier addition, barium chromate precipitation, and Cr(VI) extraction with methyl isobutyl ketone. In the third column of Table 1 a result obtained with this method is listed. As shown, close agreement, within experimental errors between the two methods is obtained.

B. DISCUSSION

The method is highly reproducible and the precision of results is about 4%. The overall error, evaluated taking into account all possible sources of error, is about 6%. The sensitivity of the described method is 0.01 μg and may be increased by irradiating, for instance, at a higher flux. The time required for the chemical separation is 1.5 hours, and the results may be obtained within 2 hours from the start of the chemical procedure.

Table 1. Chromium content of human blood serum and red cells.

Sample	Chromium content by ion exchangers method[a] (μg/ml)	Chromium content by Van Kooten [10] method[a] (μg/ml)
Blood serum	0.20	
Red cells	0.23	0.24

---

[a] The listed values are the average of duplicate analyses.

Because of the high selectivity of manganese dioxide for chromium this carrier free technique may be applied with confidence. We have checked, by analyzing an inactive blood sample to which ^{51}Cr was added in tracer amount, that chromium recovery is greater than 99% both after mineralization and after the three inorganic exchanger separations. The method may be easily extended to other biological materials and also to inorganic matrices. We have already tried it on flour.

IV. References

[1] Schroeder, M. A., J. Chron. Dis. **18,** 217 (1965).

[2] Mertx, W., and Glinsmann, W. H., Proc. 5th Congr. Int. Diabetes Federation Toronto (1964).

[3] Schroeder, M. A., Amer. J. Physiol. **207,** 1 (1964).

[4] Samsahl, K., Brune, D., and Wester, P. O., Int. J. Appl. Radiat. Isotopes **16,** 273 (1965).

[5] Wester, P. O., Acta Medica Scandinavica **178,** 6 (1965).

[6] Lesine, R. A., Streeten, D. M. P., and Daisy, R. J., Metab. Clin. Esys. **17,** 114 (1968).

[7] Pijck, J., Gillis, J., and Hoste, J., Int. J. Appl. Radiat. Isotopes **10,** 149 (1961).

[8] Samsahl, K., Nucleonics **8,** 252 (1966).

[9] Samsahl, K., Analyst **93,** 101 (1968).

[10] van Kooten, W. J., Mali, J. W. H., de Goeij, J. J. M., and Houtman, J. P. W., paper SM-91/36 presented at the IAEA Symposium on Nuclear Activation Techniques in Life Sciences, Amsterdam (1967).

[11] Bigliocca, C., Girardi F., Meloni, S., Pauly, J., Provasoli, A., and Sabbioni, E., Anal. Chem. **39,** 1634 (1967).

[12] Meloni, S., and Brandone, A., to be published in Radiochimica Acta.

[13] Meloni, S., and Brandone, A., Int. J. Appl. Radiat. Isotopes **19,** 1964 (1968).

[14] Girardi, F., Meloni, S., Sabbioni, E., Pietra I., and Brandone, A., to be published.

[15] Girardi, F., and Sabbioni, E., J. Radioanal. Chem. **1,** 169 (1968).

[16] Scientific Tables, 6th Ed. Geigy Documenta (1963).

DETERMINATION OF THE DISTRIBUTION COEFFICIENTS OF THE ELEMENTS OF THE IB, VB, VIA AND VIB GROUPS IN ANIONIC ION EXCHANGE RESIN IN THE WATER-HYDROCHLORIC ACID-ACETONE MIXTURE

Ch. Cleyrergue, N. Deschamps and Ph. Albert

CNRS – C.E.C.M.
Vitry, France

I. Introduction

The works of I. Hazan and J. Korkisch dealing with the separation of iron, cobalt and nickel by ion exchange showed that it is possible to isolate these elements on a Dowex 1 × 8 resin, using a water-acetone-hydrochloric acid mixture [1,2].

In slightly acid aqueous medium (0.5 *N* HCl) iron is very slightly absorbed on a Dowex 1 × 8 resin, nickel, cobalt, copper, and many other cations are not retained. In the case of the water-hydrochloric acid-acetone mixture, iron forms a stable complex with acetone which prevents this element from being absorbed as an anionic complex. On the contrary, nickel and cobalt are strongly absorbed by the resin.

Our purpose being the analysis of the impurities in iron by neutron activation analysis, it seemed of much interest for us to try to elute the iron which is the major radioisotope and to retain the most of the other radioisotopes on the resin column. It led us to complete the works of Korkisch *et al* and to undertake the systematic study of distribution coefficients of many ions in this medium. We were particularly interested in the elements of groups IB, VB, VIA, and VIB of the periodical classification of the elements. We are now proceeding with the determination of the distribution coefficient of other elements in this medium and also in the water-hydrochloric acid THF medium studied by J. Korkisch and S. S. Ahluwalia [2-4].

II. Experimental

A. DETERMINATION OF THE LIMIT DISTRIBUTION COEFFICIENTS

In order to determine the distribution coefficients we used the so called "static method". In this method we put a known quantity of resin in contact with a solution containing a known quantity of the studied dissolved element. The resin is stirred during a time long enough for equilibrium to be reached. We titrate the element in both phases by an appropriate method. The concentrations and then the distribution coefficients are deduced [5]. Although this method is not as precise as the "dynamic" method, it gives a satisfactory indication about the behavior of the element and has the advantage of quickness if we want to foresee the behavior of many elements. We checked the reproducibility of this method for one element and the determined values have a deviation of ±7% which is satisfactory for our study.

We studied the variation of the distribution coefficient for the following elements: As, Sb, Au, Ag, Cu, Se, Te, Mo, W as a function of the percent acetone in a 0.5 N HCl solution.

B. REAGENTS – PROCEDURE

Our experiments were carried out using radioisotopes of the studied elements. This method allows an easy measurement of the concentration of the elements on both the resin and solution. The measurements were performed by gamma spectrometry with an NaI(Tl) crystal and a multichannel pulse-height analyzer.

We used solutions of 10^{-4} M in the studied elements. To the hydrochloric solution of these elements we added acetone in order to have a 0.5 N concentration of HCl and a known concentration of acetone.

The Dowex 1 × 8, 200-400 mesh resin was previously treated with 6 N HCl and then washed with water until neutral pH and dried in air.

In a bottle which can be hermetically sealed we introduce about 1 g of this exactly weighed resin, 50 ml of the HCl-water-acetone mixture 10^{-4} M in the studied "tracer" element.

The bottle is then stirred for 24 hours.

The resin is allowed to settle, and we take an aliquot of the solution after filtration. The gamma radioactivity of this solution is determined and compared to the initial radioactivity, taking into account the decrease of the studied radioisotope. The distribution coefficient is calculated

$$K_D = \frac{A_x(\text{resin})}{A'_x(\text{solution})}$$

where A_x is the radioactivity of the element, x, on the resin per gram of dried resin, and A'_x the radioactivity of this element per milliliter of solution.

III. Results and Discussion

Figures 1 to 8 give the variation of the distribution coefficient for each element as a function of the concentration of acetone in the solution.

A. ANTIMONY

Figure 1 shows the variation of the distribution coefficient of Sb^{III}. We see that this coefficient slowly increases with the concentration of acetone but becomes quite small for a concentration of 85% acetone.

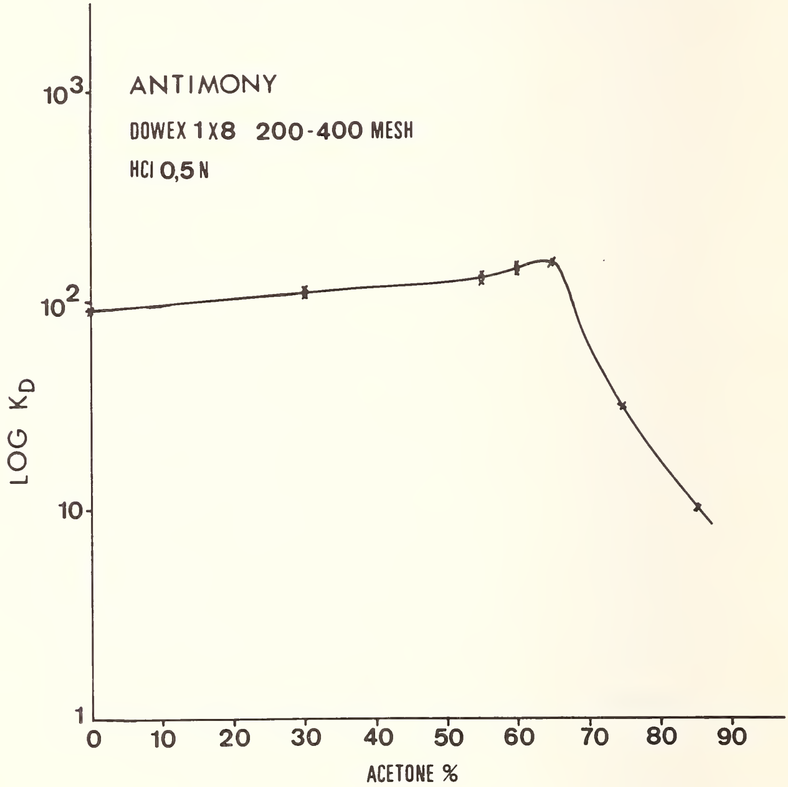

Figure 1. Variation of the distribution coefficients in water hydrochloric acid—acetone for antimony.

B. SILVER

Figure 2 shows that the distribution coefficient first decreases until a concentration of 45%, then reaches a maximum at about 60% and decreases again when the concentration of acetone increases.

We notice that the distribution coefficient always remains rather high which is identical to its behavior in hydrochloric acid medium. Nevertheless in the studied range of acidity, silver is strongly absorbed in the hydrochloric medium ($K_D > 500$) whereas it is easily eluted when acetone is present ($K_D \simeq 30$, 80% acetone).

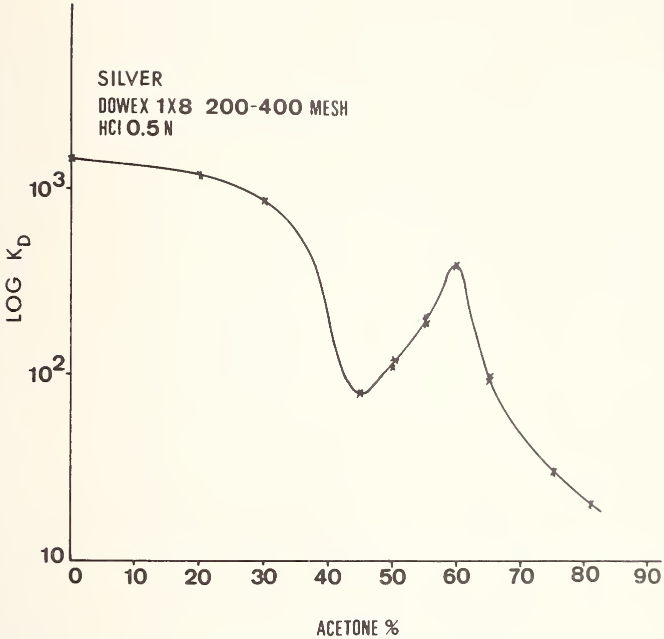

Figure 2. Variation of the distribution coefficients in water hydrochloric acid—acetone for silver.

C. Copper

Figure 3 shows a notable difference in the behavior of this element between the aqueous and mixed media. In weakly acid medium (HCl < 4 *N*) copper is not retained on Dowex 1 resin ($K_D << 10$). In the acetone-water-hydrochloric-acid medium, copper is not absorbed when the acetone concentration is less than 40% but is retained for a concentration of 60%.

D. Molybdenum

In weakly acid medium, molybdenum is not absorbed on an anion resin. Figure 4 shows that the distribution coefficient reaches a maximum value ($K_D = 30$) for a concentration of 40% acetone. Beyond this concentration the distribution coefficient decreases rapidly and becomes less than 1 over 70%.

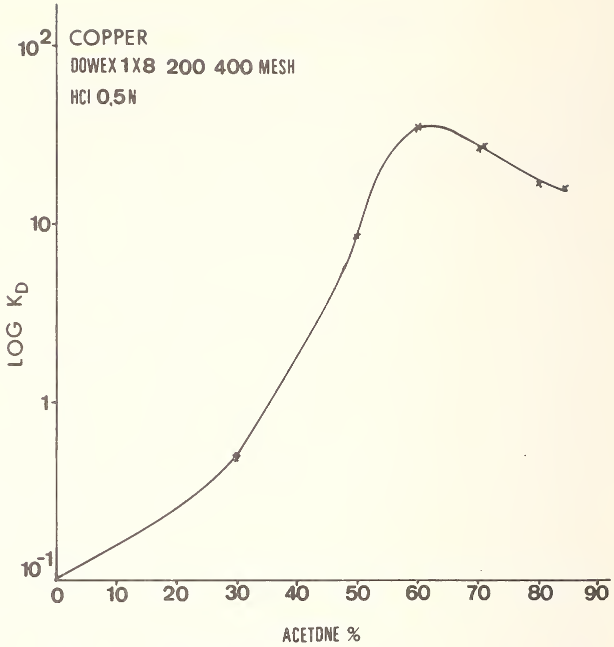

Figure 3. Variation of the distribution coefficients in water hydrochloric acid—acetone for copper.

E. Gold

The difference of gold behavior between aqueous media and water-acetone-hydrochloric acid is very important. In hydrochloric solution gold is strongly absorbed on Dowex 1 resin whatever the concentration of acid may be ($K_D > 10^4$) and particularly in a weakly acid medium ($K_D > 10^5$). Figure 5 shows that the distribution coefficient of gold decreases when the concentration of acetone increases and gold is not absorbed in the presence of 80% acetone. The low distribution coefficient of gold in this medium can be attributed to the formation of a strong complex that can be compared with the complex of iron.

F. Selenium

Figure 6 shows the variation of the distribution coefficient of selenium with the concentration of acetone in the mixture. In aqueous medium the selenium is not absorbed on the resin. On the other hand the distribution coefficient of selenium increases rapidly with the concentration of acetone and reaches a maximum value when the mixture contains 50%

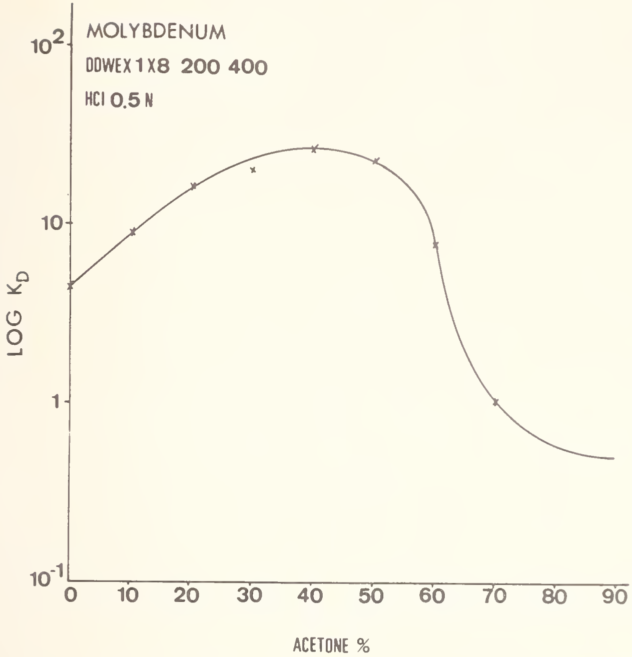

Figure 4. Variation of the distribution coefficients in water hydrochloric acid – acetone for molybdenum.

acetone. K_D is almost constant when the concentration of acetone increases.

G. Tellurium

Figure 7 shows that the behavior of tellurium is analogous with that of selenium up to a concentration of 60% acetone. On the other hand, if the proportion of acetone increases, the distribution coefficient decreases rapidly and is less than 1 in 80% acetone. Consequently, separation of selenium from tellurium is possible by use of a mixture of hydrochloric acid-acetone containing 80% acetone.

H. Tungsten

Hydrolysis of tungsten takes place in weakly acid media. Under these conditions we obtain an apparent distribution coefficient of 15 in hydrochloric acid, 0.5 *M*, and the value of K_D slightly increases with the concentration of acetone and reaches a value of 40 in the presence of 75% acetone (Fig. 8).

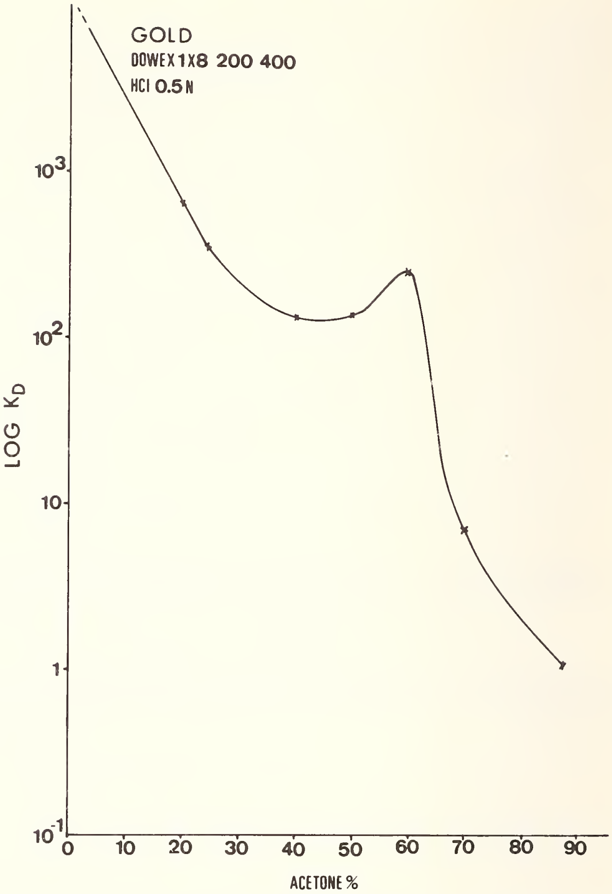

Figure 5. Variation of the distribution coefficients in water hydrochloric acid – acetone for gold.

IV. Conclusions

We have established the K_D variation curves for some elements on Dowex 1 × 8 resin in water-hydrochloric-acid-acetone mixture as a function of the concentration of acetone in the mixture. The kinetic study on the column is in good agreement with the conclusions that we can make from the K_D curves, even for tungsten.

This study allows one to consider the separation of iron from the elements of groups IB, VB, VIA and VIB. Most of these belong to the group of elements whose sulphides precipitate in diluted strong acid media. Sulphur, phosphorus, chromium and bismuth have not yet been

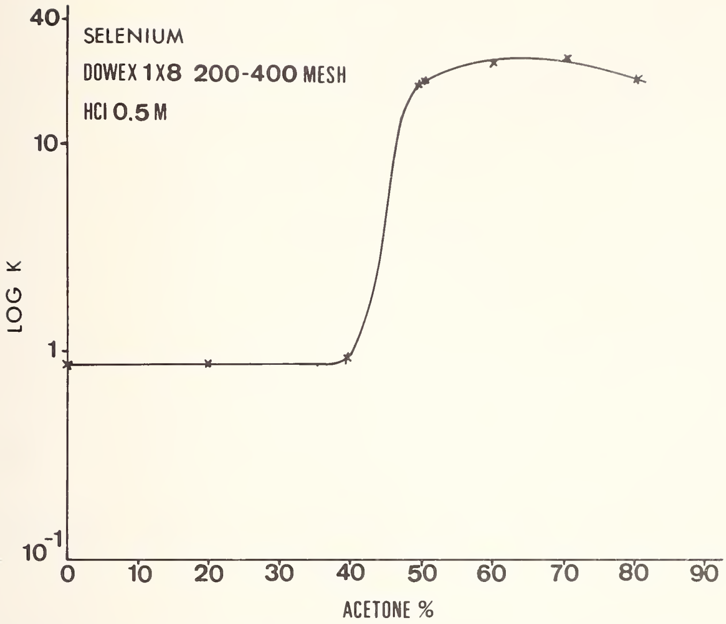

Figure 6. Variation of the distribution coefficients in water hydrochloric acid – acetone for selenium.

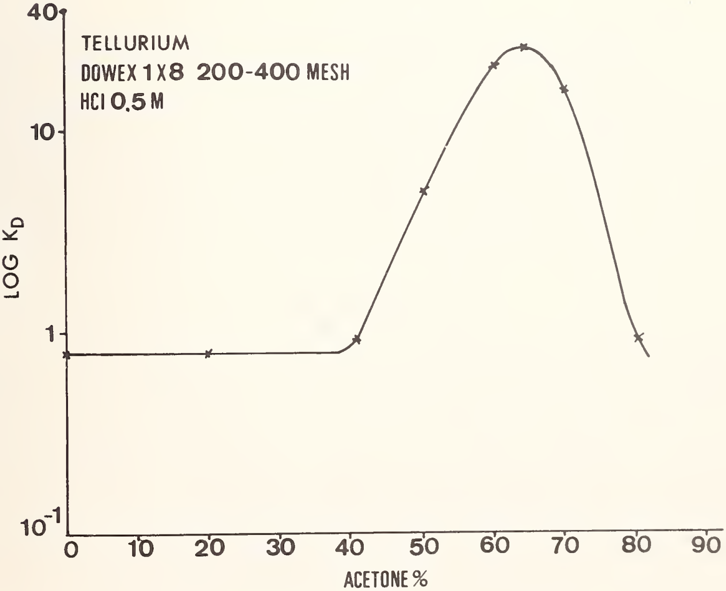

Figure 7. Variation of the distribution coefficients in water hydrochloric acid – acetone for tellurium.

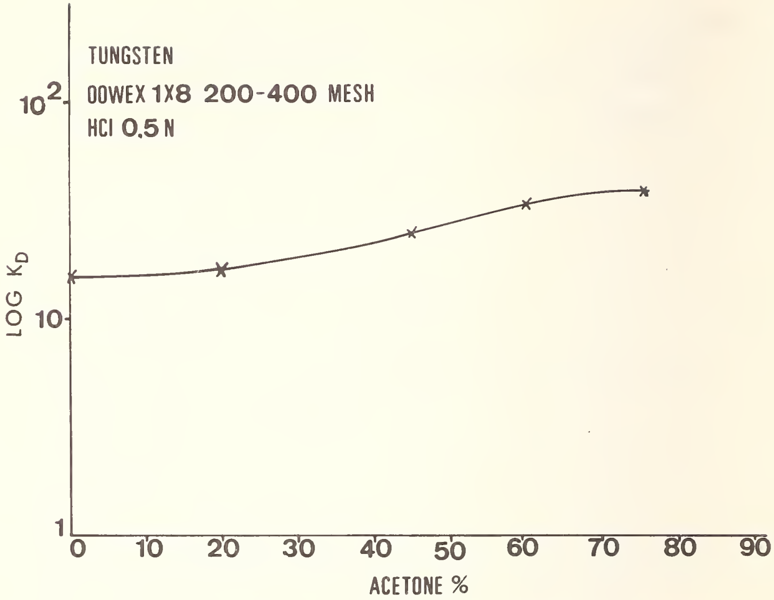

Figure 8. Variation of the distribution coefficients in water hydrochloric acid – acetone for tungsten.

studied. The former curves show that the maximum values of K_D of these elements are obtained for a concentration of acetone of approximately 60%. In these conditions, iron is slightly absorbed on the resin. We have checked that nickel and manganese are not absorbed at a concentration of 60% acetone. That is in good agreement with the results obtained by Korkisch *et al.* It is possible to apply this ion exchange method to the systematic radioactivation analysis of iron and nickel and to consider its automatization.

V. References

[1] Hazan, I., and Korkisch, J., Anal. Chim. Acta **32,** 46-51 (1965).
[2] Korkisch, J., Progress in Nuclear Energy Series IX Analytical Chemistry Vol. 6, Pergamon Press 1966, p. 36.
[3] Korkisch, J., and Ahluwalia, S. S., Anal. Chim. Acta **34,** 308-313 (1966).
[4] Korkisch, J., and Ahluwalia, S. S., Anal. Chim. Acta **38,** 49-97 (1966).
[5] Tremillon, B., Les separations par les resines echangeuses d'ions, Gauthier-Villars, Paris, 1965.

QUANTITATIVE DETERMINATION OF IMPURITIES IN NUCLEAR GRAPHITES BY RADIOACTIVATION METHODS

S. May and G. Pinte

Saclay Nuclear Research Centre
Saclay, France

I. Introduction

In this paper we describe the attempts made to try and develop a method of systematic analysis of the impurities contained in nuclear graphites. Hitherto, impurities have been determined from one sample [1-3]. We have developed a method of systematic analysis, making it possible to determine about twenty impurities in one sample. The elements found are: silver, selenium, mercury, antimony, copper, iron, gallium, cobalt, cadmium, zinc, indium, zirconium, chromium, scandium, barium, calcium, sodium, potassium, rubidium and cesium. We also mention briefly the methods used for the determination of all the rare earths, silicon, sulphur and phosphorus, as well as the elements which can be determined without chemical separation: chlorine, manganese, vanadium.

II. Experimental

A. Preparation of the Samples and Standards

The standards are prepared from pure salts and dissolved so as to obtain concentrations of 1 to 10 mg/ml. Each standard is prepared by depositing a drop of the standard solution on small extra pure aluminum foil (99.99%). After weighing and evaporation there remains 20 to 400 μg of the element. After irradiation the standards are dissolved in acid and diluted 100 times. It is also possible to evaporate 0.5 ml of the previously diluted standard solution in a small quartz flask.

The graphite samples ($\sim$10 g) are enclosed in extra pure aluminum foil. Samples and standards are placed in a cold set aluminum container. Irradiation is carried out in the EL 3 reactor of the C.E.N. Saclay in a mean flux of $1.5 \times 10^{13} \mathrm{n \cdot cm^{-2} \cdot sec^{-1}}$ for one week. For nuclear reactions (see Table 1).

B. Chemical Separation

In contrast to metals, graphite is not a substance which is easily brought into solution. The methods of dissolving it (sulphuric acid + silver

Table 1. Characteristics of the radioelements formed by (n, gamma) reaction.

Stable isotope	$\sigma \times \theta$[a]	Radioactive isotope	Half life	β lines in MeV	γ lines in MeV
^{109}Ag	1.55	^{110}Ag	252 d	0.09 (59%) 0.53 (36%)	0.656 (100%) 0.885 (81%) 0.933 (31%) 1.40 (30%)
^{74}Se	0.226	^{75}Se	120 d	E.C.	0.136 (94%) 0.270 (100%) 0.280 (46%) 0.40 (25%)
^{202}Hg	1.13	^{203}Hg	46 d	0.21	0.073–0.279
^{123}Sb	1.07	^{124}Sb	60 d	0.2 (9%) 0.61 (49%) 0.93 (4%) 1.59 (10%) 2.31 (28%)	0.60 (100%) 1.69 (52%) 2.09 (7%)
^{63}Cu	3.12	^{64}Cu	12.8 h	0.55 (39%) β+0.65 (19%)	1.34 (0.5%)
^{58}Fe	0.0036	^{59}Fe	45 d	0.27 (46%) 0.46 (54%) 1.56 (0.3%)	0.19 (2.8%) 1.10 (57%) 1.29 (43%)
^{44}Ca	0.015	^{45}Ca	165 d	0.25	– – –
^{59}Co	36.3	^{60}Co	3.3 y	0.312 (99%) 1.48 (0.01%)	1.17 (100%) 1.33 (100%)
^{114}Cd	0.04	^{115}Cd	43 d	1.62 (98%)	0.49 (60%) 0.94 (74%) 1.30 (31%)
	0.32	^{115}Cd	2.30 d	0.58 (42%) 1.11 (58%)	0.49 (14%) 0.52 (28%) 0.335 (52%)
^{64}Zn	0.23	^{65}Zn	245 d	0.324 (1.5%) E.C. (98.5%)	1.11 (44%)
^{113}In	2.38	^{114}In	50 d	E.C. (3.5%)	I.T. (96.5%) 0.19 (96.5%) 0.56 (3.6%) 0.72 (3.5%) 1.30 (0.2%)
^{94}Zr	0.0132	^{95}Zr	65 d	0.36 (54%) 0.40 (43%) 0.83 (3%)	0.72–0.216

Table 1. Characteristics of the radioelements formed by (n, gamma) reaction (continued).

Stable isotope	$\sigma \times \theta^a$	Radioactive isotope	Half life	β lines in MeV	γ lines in MeV
^{50}Cr	0.685	^{51}Cr	27.8 d	E.C.	0.325 (9%)
^{45}Sc	22.3	^{46}Sc	84 d	0.36 (100%) 1.25 (0.004%)	0.89 (98%) 1.12 (100%)
^{130}Ba	---	^{131}Ba	12 d	E.C.	0.124 (28%) 0.216 (19%) 0.25 (5%) 0.373 (13%) 0.496 (48%) 0.60 (3%) 0.924 (0.9%) 1.048 (1.3%)
^{71}Ga	2	^{72}Ga	14 h	0.64 (42%) 0.96 (31%) 1.51 (10%) 2.53 (9%) 3.14 (8%)	0.63 (21%) 0.833 (93%) 1.05 (7%) 1.25 (71%) 2.21 (30%) 2.50 (27%)
^{23}Na	0.54	^{24}Na	15 h	1.39 (100%)	1.37 (100%) 2.76 (100%)
^{41}K	0.09	^{42}K	12.5 h	2.04 (25%) 3.58 (75%)	1.51 (25%)
^{85}Rb	0.655	^{86}Rb	18.7 d	0.71 (15%) 1.78 (84%)	1.08 (8.8%)
^{133}Cs	33	^{134}Cs	2.2 y	0.657 (81%)	1.37 (5%) 1.17 (3%) 1.05 (4%) 0.80 (36%) 0.605 (100%)

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[a] σ = cross section in barns

θ = isotopic abundance

dichromate for example) are generally very long and do not suit all graphites.

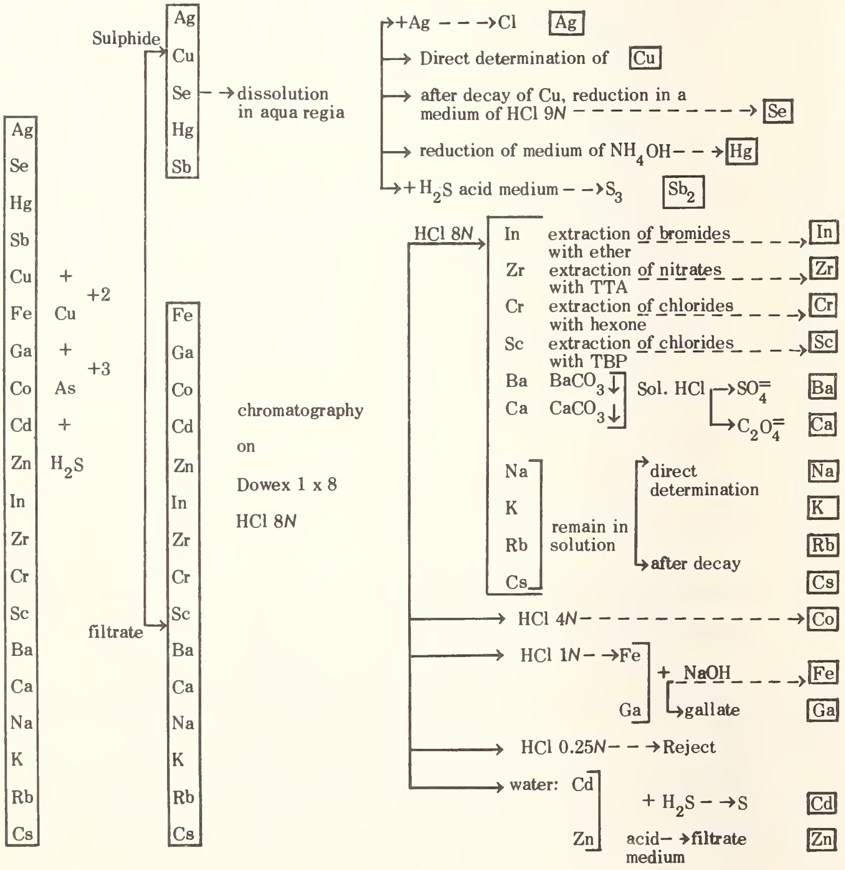
Previous studies had shown that the impurities of nuclear graphites are located for the most part in the pores [1,2]. Therefore we did not attempt to dissolve the graphite completely, but to extract the impurities by an appropriate acid.

After various tests, fuming nitric acid proved to be the most satisfactory for the impurities. After irradiation and elimination of external contamination, the graphite sample is crushed in a tungsten carbide mortar. Extraction is achieved by reflux heating in the presence of fuming nitric acid (5 g of graphite + 100 ml HNO_3 for 2 hours). After three extraction cycles, there remains about 0.5% of the initial activity due to the presence of radiotantalum and a little radiocobalt and radiosodium.

1. *Systematic Separation*

The different stages of the operations are summarized in Table 2. We determined the chemical separation yield of the elements determined.

Table 2. General separation flowsheet.



These yields apply to the nitric solutions collected after extraction of the impurities from the graphites:

Ag = 90 ± 5%,
Sb = 89 ± 5%,
Zr = 92 ± 3%,
Cd = 85 ± 5%,
Ba = 81 ± 6%,
Ga = 85 ± 5%,
Se = 75 ± 5%,
Hg = 80 ± 5%,
Fe = 97 ± 2%,
Cr = 92 ± 4%,
In = 90 ± 5%,
Co = 94 ± 3%,
Sc = 88 ± 3%,
Zn = 85 ± 5%
Rb = 80 ± 8%
Cs = 89 ± 4%
Cu = 93 ± 5%
Ca = 75 ± 5%
Na = 90 ± 6%
K = 85 ± 10%

The solution containing the impurities extracted in a nitric medium is concentrated and then placed in a hydrochloric medium. It is saturated with H_2S after addition of the carriers copper and arsenic. The sulphides of copper and arsenic carry the elements Se, Ag, Hg, Sb and Cu by coprecipitation. After filtration, the filtrate contains the elements: Fe, Ga, Co, Cd, Zn, In, Zr, Cr, Sc, Ba, Ca, Na, K, Rb, and Cs.

2. *Treatment of Arsenic and Copper Sulphides*

The sulphides are dissolved in a minimum of aqua regia. After concentration, the solution is diluted. After the addition of carrier, Ag is precipitated in the form of AgCl. Copper can be determined directly by gamma spectrometry. After decay, Se, Hg and Sb can be determined. Se is precipitated by a solution of hydrazine hydrochloride saturated with SO_2, in a hydrochloric medium [5] and Hg is precipitated by the same reagent in an ammoniacal medium. Sb is then separated in the form Sb_2S_3.

3. *Treatment of the Sulphide Filtrate*

The elements remaining in the sulphide filtrate are separated by chromatography on Dowex ion exchange resin 1 × 8, 100-200 Mesh in the form H^+ (column 25 cm long and 1 cm^2 in section). The elements are fixed in a 9 *N* HCl medium. Elution is achieved by: (1) 8 *N* HCl: In, Zr, Cr, Sc, Ba, Na, K, Rb, Cs are eluted. (2) 4 *N* HCl: Co is eluted. (3) 1 *N* HCl: Fe and Ga are eluted. They are extracted in a 9 *N* HCl medium by isopropyl ester, reextracted by H_2O. Fe is precipitated in the form of hydroxide. Ga remains in solution in the form of sodium gallate. (4) 0.3 *N* HCl: Rejected fraction. (5) H_2O: Cd and Zn are eluted. Cd is precipitated by H_2S in hydrochloric medium. Zn remains in solution.

4. *Treatment of the Eluted Fraction by 8 N HCl*

In is extracted in hydrobromic medium by ethyl ester and coprecipitated on $Fe(OH)_3$. Zr is separated in a nitric medium by extraction with thenoyltrifluoroacetone (TTA) in xylene. Cr^{+3} is oxidized to Cr^{+6} and extracted with hexone in a hydrochloric medium. Sc is then coprecipitated with $Fe(OH)_3$ in an ammoniacal medium and then extracted by tributyl phosphate (TBP) in an acid medium. Ba and Ca are separated by precipitation of the carbonates. Ba is precipitated in the form of sulphate and Ca in the form of oxalate. Na and K are determined simultaneously by gamma spectrometry. After decay of Na* and K*, Rb and Cs can be determined without separation, their gamma lines being clearly differentiated.

III. Results

The main results are summarized in Table 3. The gamma measurements are made with the aid of a gamma-spectrometer assembly fitted with a 400 channel analyzer and an NaI(Tl) 3 in. × 3 in. probe.

Table 3. Concentrations found in different graphites.[a]

Element	EDF 3 graphite	G2–G3 graphite	Regular coke graphite
Silver	2.2×10^{-4}	2.8×10^{-4}	$< 3.3 \times 10^{-4}$
Selenium	0.3×10^{-3}	0.8×10^{-3}	0.8×10^{-3}
Mercury	0.94×10^{-2}	7.6	3.1×10^{-2}
Antimony	1.3×10^{-3}	0.56×10^{-3}	4×10^{-3}
Copper	0.10	1.05	3.8×10^{-2}
Iron	1.9	1.25	3.5
Gallium	$< 10^{-3}$	$< 10^{-3}$	$< 3 \times 10^{-3}$
Cobalt	1.5×10^{-2}	1.06×10^{-2}	5.3×10^{-2}
Cadmium	0.85×10^{-2}	1.4×10^{-2}	$< 5 \times 10^{-2}$
Zinc	0.21	0.1	2.5×10^{-2}
Indium	1.1×10^{-4}	4.4×10^{-4}	$< 2 \times 10^{-3}$
Zirconium	3×10^{-2}	0.33	$< 2 \times 10^{-2}$
Chromium	0.1	9.5×10^{-2}	0.61
Scandium	0.19×10^{-3}	0.34	2.3×10^{-3}
Calcium	2.9	17	5.2
Sodium	0.21	11	0.25
Potassium	1.2	27	0.7; 1.5
Rubidium	1.5×10^{-2}	2×10^{-2}	1.1×10^{-3}
Cesium	1.26×10^{-3}	1.2×10^{-3}	1.3×10^{-3}

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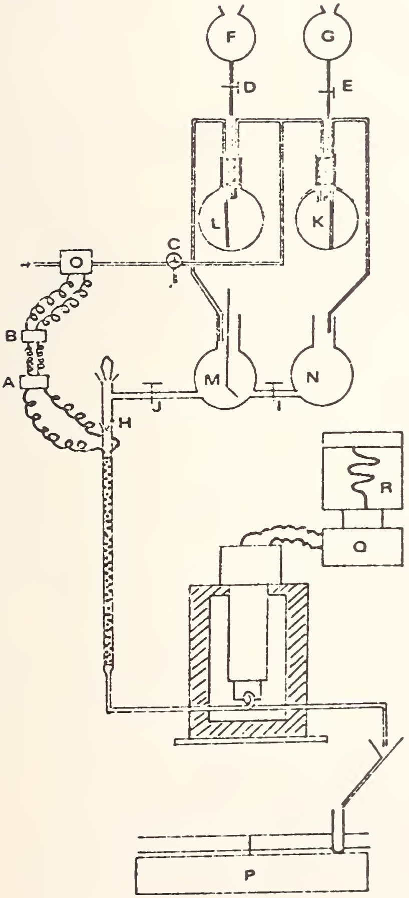
[a] Results expressed in ppm (10^{-6}).

A. DETERMINATION OF RARE EARTHS AND THE ELEMENTS V, NA, MN, CL, SI, S AND P

1. Rare Earths

The ashes of graphites (after combustion of the graphite at 850 °C) are made soluble by $HClO_4$ then by HNO_3. The rare earths coprecipitated with $Fe(OH)_3$ are irradiated at a flux of about $10^{14} n \cdot cm^{-2} \cdot sec^{-1}$. After carrying on lanthanum separation is carried out on Dowex resin 50 W × 8, 200-400 Mesh with elution by alphahydroxyisobutyric acid with two pH gradients (see Fig. 1). Each rare earth is identified by gamma spectrometry (see Table 7). Some results are given in Table 4.



A – Electronic control of sensitive relay
B – Power relay
C – 3-way valve
D – Bromine flask valve
E – Bromine flask valve
F – Filling reservoir
G – Filling reservoir
H – Ground joint
I – Mixer valve
J – Mixer valve
K – Reserve reservoir
L – Reserve reservoir
M – Mixer vessel
N – Storage vessel
O – Solenoid valve
P – Fraction collector
Q – Integrator
R – Recorder

Figure 1. Diagram of apparatus.

Table 4. Analysis of rare earths in nuclear graphites.[a]

	OP 3607–3	CD 37.875	OP 3607–1	OP 3607–2	OP 3607–5	CEA 3643–1	CEA 3542–1
Lutetium	4.3×10^{-2}	6.9×10^{-1}	4.4×10^{-2}	4.1×10^{-2}	3.5×10^{-2}	1.8×10^{-2}	– – –
Ytterbium	4.2×10^{-1}	2.5	3.1×10^{-1}	5.9×10^{-1}	5.3×10^{-1}	3.3×10^{-1}	– – –
Thulium	– – –	8.8×10^{-1}	– – –	– – –	– – –	– – –	– – –
Erbium	– – –	18.7	1.6	9.2×10^{-1}	2×10^{-1}	9.7×10^{-1}	4.1
Holmium	5.6×10^{-2}	4.9	4×10^{-1}	1.9×10^{-1}	2.2×10^{-1}	9.5×10^{-2}	8.3×10^{-1}
Dysprosium	7.5×10^{-1}	14	7.5	6.7×10^{-1}	– – –	– – –	– – –
Terbium	10^{-1}	1.8	2×10^{-1}	10^{-1}	1.8×10^{-1}	1.3×10^{-1}	3.8×10^{-1}
Gadolinium	7.8×10^{-1}	39.3	5.1	2.7	1.7	1.4	15.3
Europium	5.1×10^{-1}	5.1	8.9×10^{-1}	1.8	6.2×10^{-1}	1.2×10^{-1}	4.3
Samarium	1.5	12	1.7	3.2	1.9	1.1	11.2
Neodymium	3.2×10^{-3}	3.4×10^{-2}	6.3×10^{-3}	3×10^{-3}	5.2×10^{-3}	3.5×10^{-3}	10^{-2}
Praseodymium	1.3	31.3	5.4×10^{-1}	3.9	3.3	1.6	18.5
Cerium	3.6	112	2.2	13.2	8.7	7.2	30
Lanthanum	4.5	42.6	14.5	6.7	4.4	2.5	10.3

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[a] Results expressed in ppb (10^{-9}).

2. *V, Na, Mn, Cl, Si, S and P*

The elements V, Na, Mn and Cl can be determined without chemical separation (characteristics in Table 5) by computer. Finally, the elements Si [5] S and P [3] can be determined separately with appropriate chemical separation (see Table 6).

Table 5. Nuclear characteristics of the elements chlorine, manganese, sodium and vanadium (n, γ) reactions.

Natural radioisotope	Isotopic abundance (%)	Radioelement formed	Half life	Energies in MeV β	γ
^{37}Cl	24.6	^{38}Cl	38.5 min	1.11	1.60
				2.77	2.15
				4.81	
^{55}Mn	100	^{56}Mn	2.6 h	0.73	0.845
				1.05	1.81
				2.86	2.13
^{23}Na	100	^{24}Na	14.9 h	1.39	1.38
					2.76
^{51}V	100	^{52}V	3.76 min	2.47	1.44

Table 6. Isotopes of silicon formed by (n, γ) reaction; isotopes of sulfur formed by (n, γ) and (n, p) reactions.

Natural isotope	Isotopic abundance (%)	Cross section (barn)	Isotope produced	Half life	Emitter
		Silicon (n, γ) reaction			
^{28}Si	92.27	0.08	^{29}Si	stable	
^{29}Si	1.68	0.28	^{30}Si	stable	
^{30}Si	3.05	0.11	^{31}Si	2.62 h	β^- 1.47 MeV
		Sulfur (n, γ) reaction			
^{34}S	4.2	0.26	^{35}S	87 d	β^- 0.167 MeV
^{36}S	0.017	0.14	^{37}S	5 min	β^- 1.6 4.3 MeV γ 3.09 MeV
		Sulfur (n, p) reaction			
^{32}S	95	0.06	^{32}p	14.5 d	β^- 1.71 MeV
^{33}S	0.75	0.002	^{33}p	25 d	β^- 0.25 MeV

Table 7. Nuclear characteristics of rare earths.

Natural element	Isotopic abundance (%)	Cross section (barn)	Radionuclide formed	Half life	Most important gamma-ray lines (MeV)
^{139}La	99.91	8.9	^{140}La	40.2 h	0.33, 0.49, 0.82, $\underline{1.60}$, 2.53
^{142}Ce	11.07	1	^{143}Ce	33 h	0.036, $\underline{0.294}$
^{141}Pr	100	11	^{142}Pr	19.2 h	$\underline{1.57}$
^{146}Nd	17.18	2	^{147}Nd	11.3 d	0.038, 0.091, 0.322, $\underline{0.533}$
^{152}Sm	26.63	140	^{153}Sm	47 h	0.013, 0.041, 0.070, $\underline{0.102}$
^{151}Eu	47.77	1,400	^{152}Eu	9.2 h	0.040, 0.122, 0.34, $\underline{0.837}$, $\underline{0.961}$
^{158}Gd	24,87	4	^{159}Gd	18 h	0.044, $\underline{0.364}$
^{159}Tb	100	43	^{160}Tb	73 d	0.086, 0.299, $\underline{0.880}$, $\underline{0.970}$
^{164}Dy	28.18	2,600	^{165}Dy	2.32 d	0.047, 0.093, 0.285, $\underline{0.370}$
^{165}Ho	100	64	^{166}Ho	27.3 h	0.047, 0.080, $\underline{1.36}$
^{170}Er	14.88	9	^{171}Er	7.5 h	0.051, 0.112, $\underline{0.308}$
^{169}Tm	100	125	^{170}Tm	129 d	0.024, 0.052, $\underline{0.084}$
^{174}Yb	31.84	60	^{175}Yb	4.2 d	0.053, 0.144, 0.283, $\underline{0.396}$
^{176}Lu	2.60	3,200	^{177}Lu	6.8 d	0.027, 0.055, 0.113, $\underline{0.208}$

IV. Conclusions

We now have neutron activation analytical techniques in nuclear graphites for 41 elements, 34 of which can be determined by systematic analyses. The techniques which we have developed demonstrate the value of activation analysis applied to the determination of impurities in a material which is difficult to analyze such as nuclear graphite.

V. References

[1] May, S., Bull. Soc. Chim., 2203-08 (1961).
[2] Lang, F. M., Magnier, P., May, S., Pinte, G., J. Chim. Phys. **47**, (1967).
[3] May, S., and Piccot, D., Radiochemical Methods of Analysis Vol. I, p. 137, International Atomic Energy Agency, Vienna (1965).
[4] Falcoff, R., May, S., Piccot, D., Bull. Soc. Chim. 9-3257-66 (1967).
[5] May, S., and Piccot, D., Bull. Soc. Chim. 1-332-35 (1966).
[6] Gaittet, J., These Ann. Chim. Serie A-3 1219 (1960).

RADIOCHEMICAL SEPARATIONS FOR ACTIVATION ANALYSIS USING BIS(2-ETHYL-HEXYL) ORTHOPHOSPHORIC ACID

I. H. Qureshi,[1] L. T. McClendon and P. D. LaFleur

Analytical Chemistry Division
National Bureau of Standards
Washington, D.C. 20234

I. Introduction

The reagent bis(2-ethyl-hexyl) orthophosphoric acid (abbreviated HDEHP) has been widely used as an extractant for the separations of the lanthanides and actinides [1-4] but its use as an extractant for other elements has not been studied extensively. Although extraction of a number of elements into HDEHP from dilute hydrochloric acid has been studied [5], no comprehensive investigations have been made on extraction from mineral acids at concentrations greater than 2-3M. Very often in activation analysis the need arises to perform chemical separation from a matrix that is much more acidic than 2M. Therefore, we believe that the applicability of this reagent to separations chemistry can be greatly increased by working in strong acid media ($>1M$) and that it may be applied for group chemical separations in activation analysis. Therefore, a comprehensive investigation was begun to study the extraction of metal ions into HDEHP from 1M to 11M nitric, hydrochloric and perchloric acids.

II. Experimental

A. Apparatus and Reagents

The extractions were performed in 35 ml round bottom centrifuge tubes equipped with conical-polyethylene line screw caps. A mechanical shaker was used to mix the phases during extraction, and a scintillation counter having an automatic sample changer was used for the radioassay of the samples.

HDEHP obtained from commercial sources was purified according to the procedure of Schmitt and Blake [6]. The purified reagent was >99.5% pure. The radiochemical purity of all the tracers used in this study was checked by gamma-ray spectrometry. In all the extraction studies the amount of nonradioactive carrier of the element being studied was less than 100 μg.

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[1] Present address: Pakistan Atomic Energy Commission, P.O. Box 3112, Karachi, Pakistan.

B. PROCEDURE

In a centrifuge tube 9.9 ml of the acid and 0.1 ml of the tracer of the desired element were placed and the tracer was thoroughly mixed with the acid by vigorously agitating the tube. Exactly 10 ml of 0.75*M* HDEHP in cyclohexane was added and the sample was mechanically agitated for 4 minutes (this time is sufficient for equilibrium to be attained [7,8]). The sample was then centrifuged to assure phase separation. Exactly one milliliter aliquots of the organic and the aqueous phases were transferred to glass counting tubes for radioassay. Activities of the samples were corrected for radioactive decay whenever necessary. The samples were analyzed in triplicate. In all cases a 0.1-ml aliquot of the tracer solution was counted to make sure that no anomalous effects, such as precipitation on the walls of the extraction vessel had occurred.

III. Results and Discussion

The distribution coefficient and the percent extraction of the elements studied were determined radiochemically from 1*M* to 11*M*, nitric, hydrochloric and perchloric acids into HDEHP. The percent extraction of these elements is shown in Figures 1 to 3 as a function of acid concentration.

The extraction of metal ions into HDEHP is generally expressed by the following reaction.

$$M^{+n}_{aq} + n(HG)_{2\,org} \rightleftarrows M(HG_2)_{n\,org} + nH^{+}_{aq} \qquad (1)$$

where M is the metal ion and $(HG)_2$ represents a dimeric molecule of HDEHP. For relatively weak metal-organic complexes, the hydrogen ion can compete effectively for the reagent and the metal extraction would decrease with increasing acidity as may be seen from the figures. However, for elements which form strong complexes with HDEHP, increasing acidity should have little or no effect in their extraction, as is observed in the case of group IVB elements.

The enhanced extraction of certain elements studied at acid concentration above 5*M*, especially in perchloric and nitric acids, suggests a change in extraction mechanism. This behavior could most likely be explained by either (or both) of the following two mechanisms. First, the formation of more highly associated complexes to form polymeric species as reported by Baes *et al* [8], and secondly, the mineral acid or its anion may be involved and may be represented by the equations,

$$M^{n}_{aq} + mX^{-}_{aq} + n(HG)_{2\,org} \rightleftarrows MX_m(HG_2)_{n-m\,org} \qquad (2)$$

$$M^{+n}_{aq} + mHX_{aq} + n(HG)_{2\,org} \rightleftarrows M(HX)_m(HG)_{n-m\,org} + (n-m)H^{+} \qquad (3)$$

where X^- represents the anion of an acid.

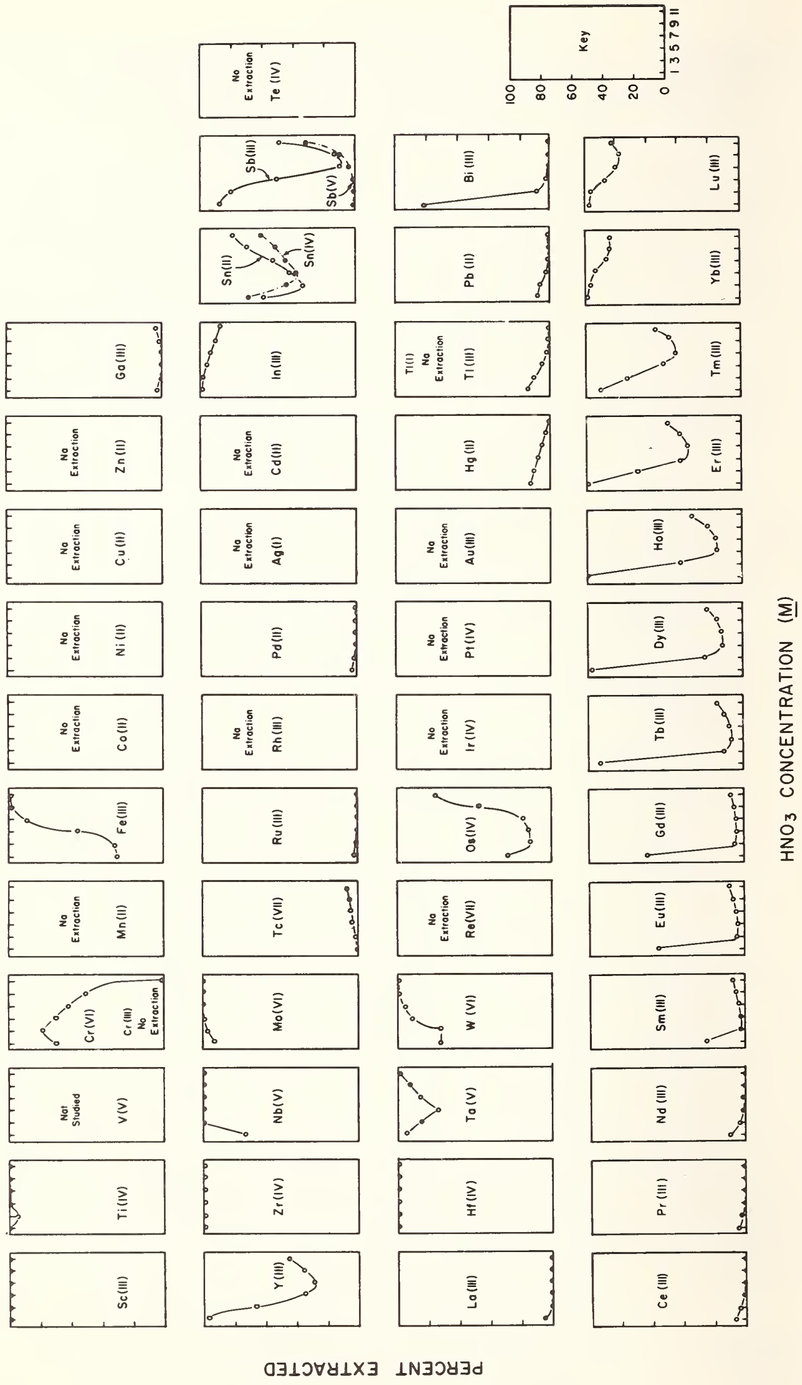

Figure 1. Extraction of metals into HDEHP as a function of nitric acid concentration.

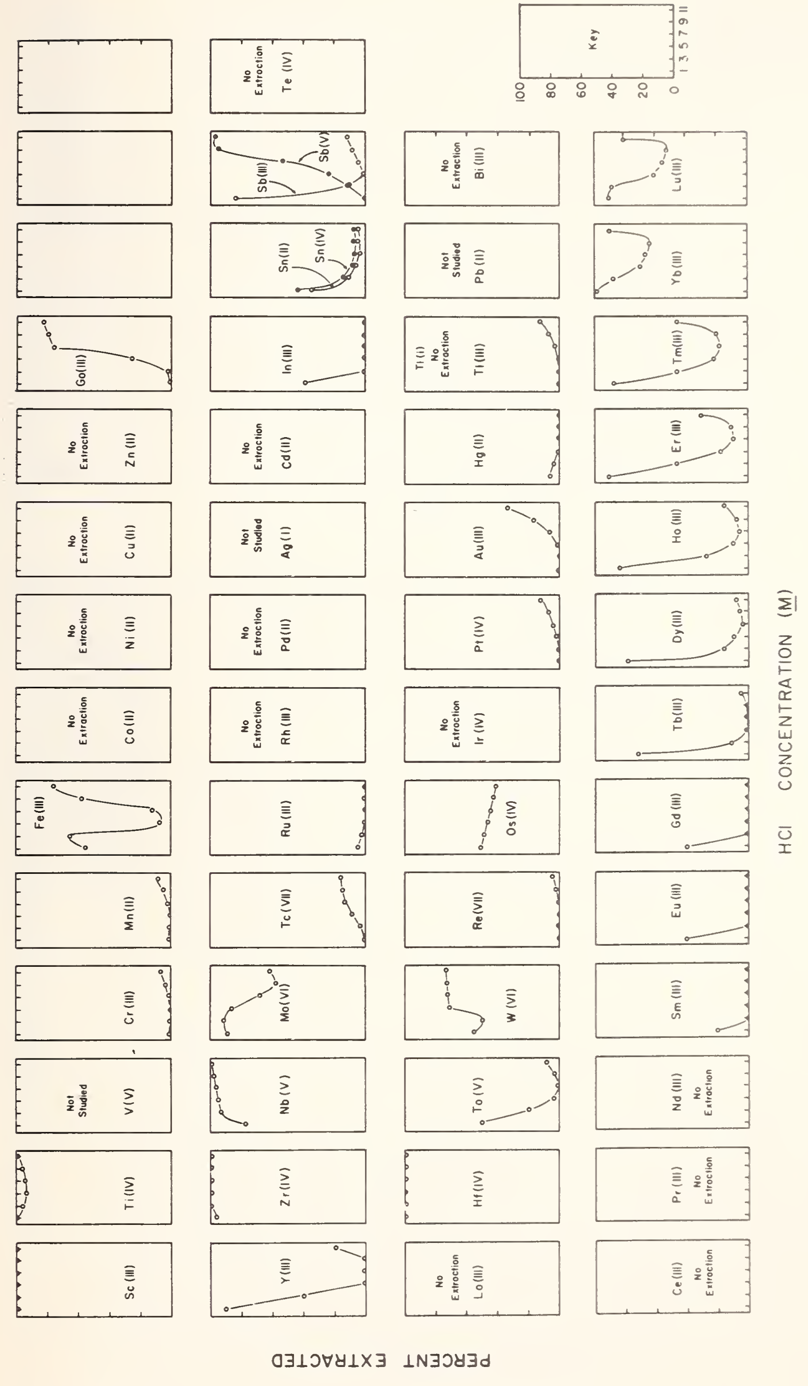

Figure 2. Extraction of metals into HDEHP as a function of hydrochloric acid concentration.

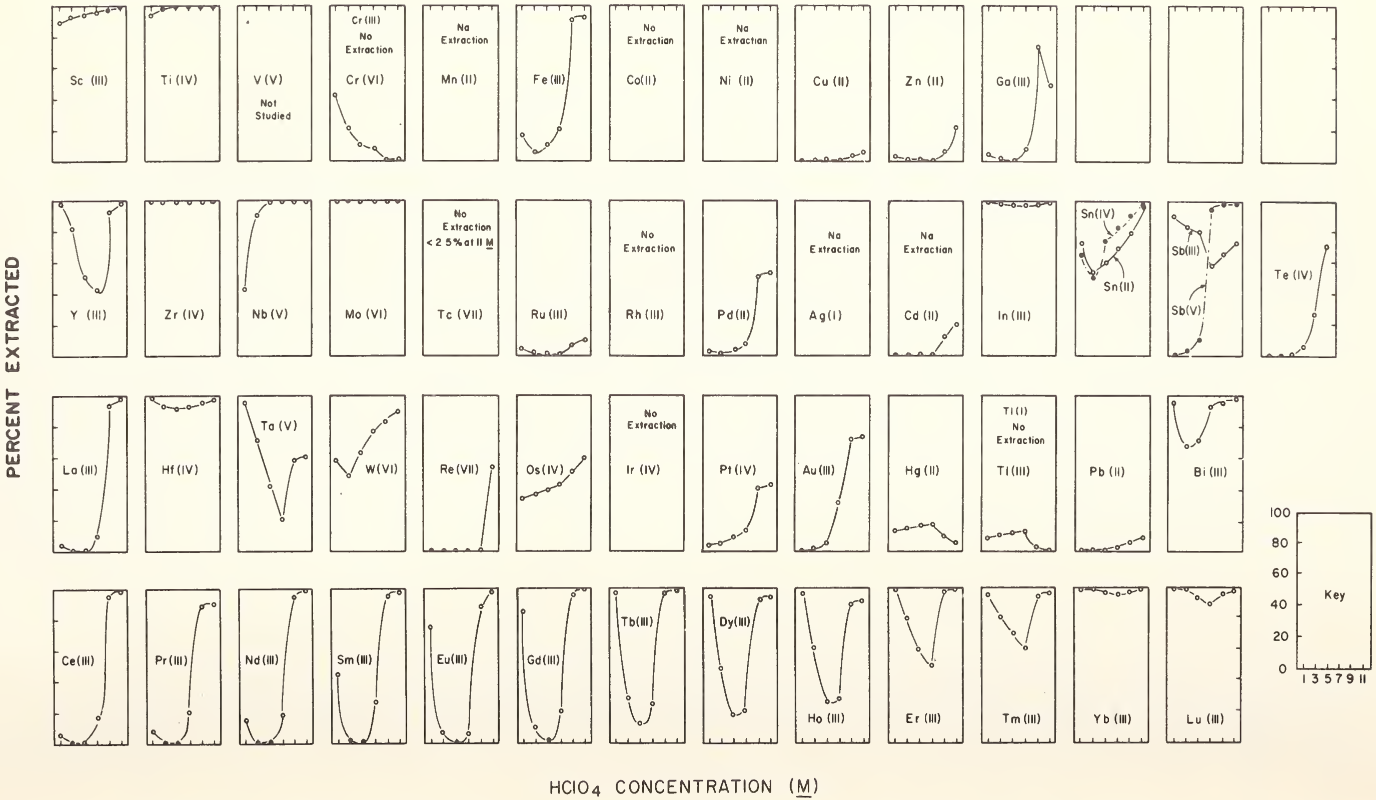

Figure 3. Extraction of metals into HDEHP as a function of perchloric acid concentration.

Our preliminary studies indicate that both nitric and perchloric acids participate in the extraction at concentration greater than $5M$ which corresponds quite closely to the point where enhanced extraction is noted.

This study clearly indicates that bis(2-ethyl-hexyl) phosphoric is a useful extractant, and appears to hold excellent promise for group chemical separations.

An early application of this reagent to activation analysis has been developed for the determination of cerium and molybdenum in the NBS Standard Reference Steel samples. More recently it has been applied to the determination of cerium, molybdenum and scandium in the U.S. Geological Survey Standard Rock samples. The three elements were extracted from $5M$ HNO_3 (containing $1M$ $NaBrO_3$). Cerium and molybdenum were separated by sequential stripping with $3M$ $HClO_4$ + hydroquinone and $10M$ $HNO_3 + 3\%$ H_2O_2 solutions respectively.

IV. References

[1] Peppard, D. F., Mason, G. W., Maier, J. L., and Driscoll, W. J., J. Inorg. Nucl. Chem. **4,** 334 (1957).

[2] Peppard, D. F., Mason, G. W., Driscoll, W. J., and Sironen, R. J., *ibid.* **7,** 276 (1958).

[3] Blake, C. A., Jr., Baes, C. F., Jr., Brown, K. B., Coleman, C. F., and White, J. C., Proc. 2nd Int. Conf. on "Peaceful Uses of Atomic Energy." A/Conf. 15/p/1550, 1958.

[4] Peppard, D. F., Mason, G. W., and Andrejasick, C. M., J. Inorg. Nucl. Chem. **25,** 1175 (1963).

[5] Kimura, K., Bull. Chem. Soc. Japan **33,** 1038 (1960).

[6] Schmitt, J. M., and Blake, C. A., Jr., USAEC Report, ORNL-3548, 1964.

[7] Peppard, D. F., and Farraro, J. R., J. Inorg. Nucl. Chem. **10,** 275 (1959).

[8] Baes, C. F., Jr., Zingaro, R. A., and Coleman, C. F., J. Phys. Chem. **62,** 129 (1958).

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